

PYROLYSIS OF SOME CYCLOBUTANE DERIVATIVES

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INDEX

	<u>Page</u>
INTRODUCTION	1
DISCUSSION	12
EXPERIMENTAL	44
REFERENCES	64
ACKNOWLEDGEMENT	68
COMPOUND INDEX	69

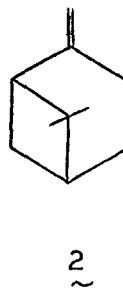
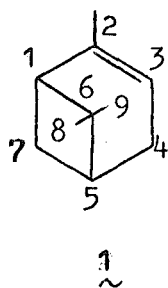
ABSTRACT

The pyrolysis of 10 β -pinane-2,3 α -diol 48, 10 β -pinane-2,10-diol 47, 2,3-epoxy-10 β -pinane 51 and 2,10-epoxy-10 β -pinane 57 are described. The products result from (C2)-O bond cleavage and there is a marked similarity in product mixtures between the corresponding diols and epoxides.

Mixtures of cis- and trans- 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutanes (64 and 65) and cis- and trans- 2,2-dimethyl-1-(2-methoxyethyl)-3-methoxymethylcyclobutanes (72 and 73) were pyrolysed at temperatures greater than 600°C. The configuration at C(1) and C(3) was found to be important in determining the path of cyclobutane cleavage. The trans-compounds 65 and 73 showed a marked bias to give products resulting from cleavage of the C-C bond adjacent to the axial substituent.

INTRODUCTION

Turpentine, a by-product of the Kraft wood pulping process contains as the main constituents, α -pinene 1 and β -pinene 2.



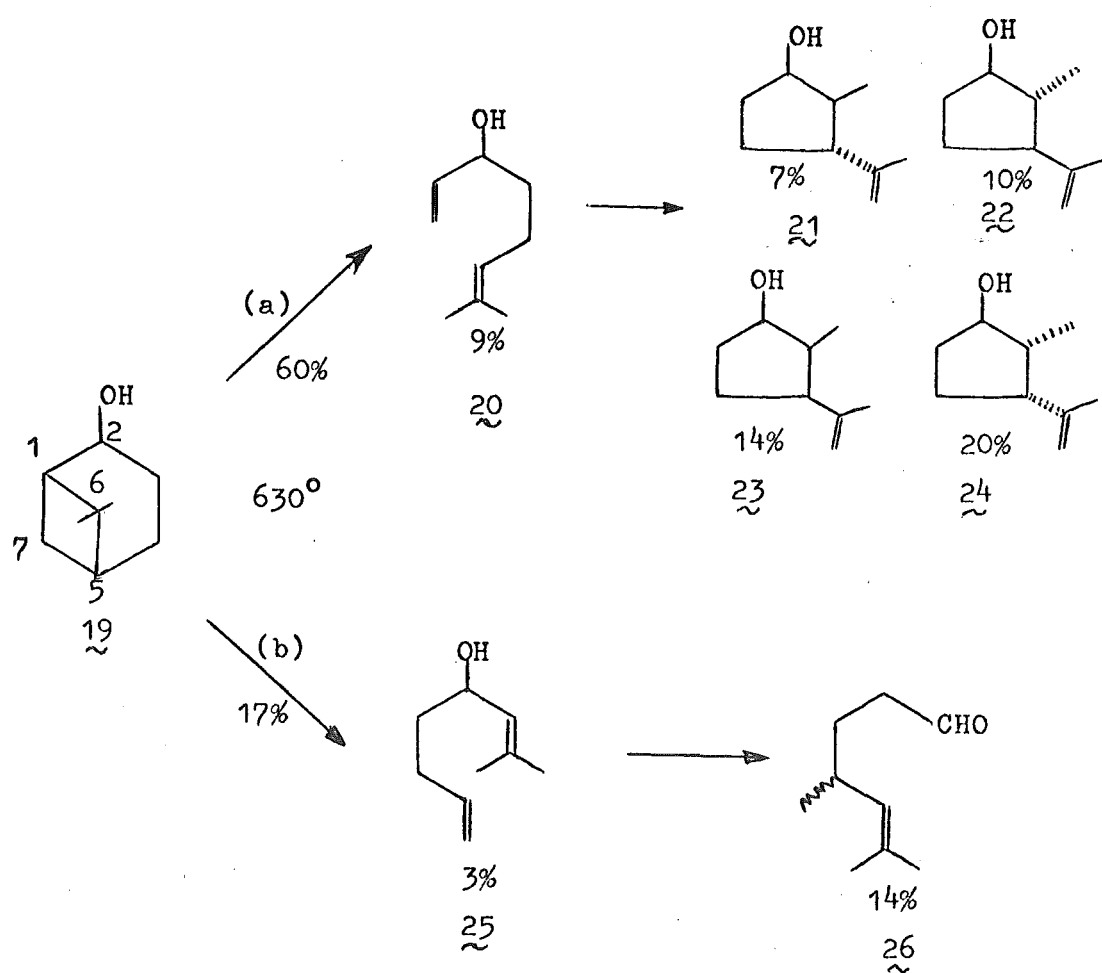
At Canterbury University, a study has been directed towards the commercial utilization of α - and β - pinene. New Zealand's turpentine is rich in the more valuable pinene, β -pinene (>65% c.f. 10 - 35% for North American turpentine). Until fairly recently, a large proportion of N.Z. turpentine was burnt. Today α -pinene is converted to α -terpeniol 7 and there is interest in further chemical processes utilizing the comparative advantage of turpentine enriched in β -pinene.

Interest in the thermal reactions of pinane derivatives began in 1841 when Gay-Lussac and Larivere¹ found that turpentine when heated produced some oils more volatile and others less volatile than the starting turpentine. It was in 1935 when the products of α -pinene pyrolysis were first isolated by Dupont². α -Pinene was passed over copper gauze at 300 - 350°C, resulting in products identified as dipentene 3, allo-ocimene 4 and α - and β - pyronene 5 and 6. A few years later, α -pinene was passed over an electrically heated platinum spiral to produce isoprene 8

(26%)³. Many workers varied the conditions of pyrolysis in attempts to produce a reaction of industrial applicability. The only other product they isolated however, was the precursor of allo-ocimene 4, namely ocimene 9⁴.

In 1941, β -pinene was pyrolysed⁵ at 375°C and the two main products were identified as myrcene 10 (67%), and limonene 3 (13%). The two minor products which were later isolated were, 1(7), 8-p-menthadiene 11, (5%)⁶, and α -myrcene 12⁷. At high temperature and short contact time, myrcene 10 is produced in 85% yield from a continuous pyrolysis process. Tonnage quantities of myrcene 10 are now used for the production of perfumery compounds such as geraniol 13, nerol 14, linalool 15, and citronellol 16. Large quantities are also used to produce the citrals 17 and 18, which are used as flavouring agents and also as precursors in the production of vitamin A. These valuable compounds are all oxygenated derivatives of myrcene. The possibility of producing these types of compounds directly by the pyrolysis of oxygenated pinanes has resulted in the present interest.

Most of the pyrolysis reactions have not been studied in any detail until fairly recently. The products formed from the pyrolysis of pinane derivatives generally result from the cleavage of the C(1),C(6) or C(1),C(6) and C(5),C(7) bonds of the pinane cyclobutane ring. The pyrolysis of nopinol⁸ 19 however gave in addition to products of normal C(1),C(6) and C(1),C(6) - C(5),C(7) cleavage, primary and secondary products via C(5),C(6) and C(1),C(7) bond cleavage. (Scheme 1). The two cleavage paths (a) and (b) resulting from the dissymmetry of this molecule

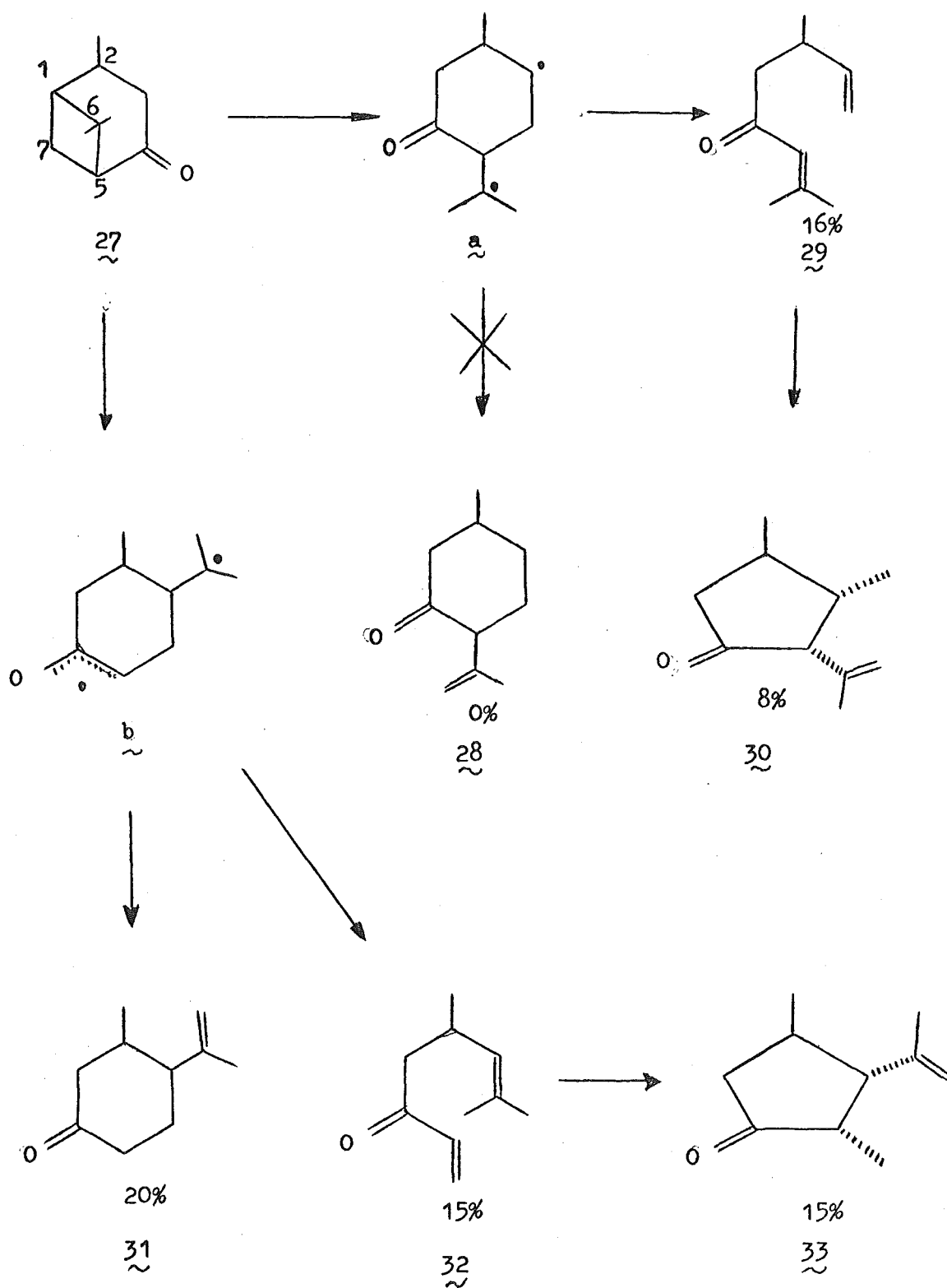
Scheme 1

allow a measure of substituent effect (2 β OH vs 4 β H) on the thermal fragmentation of the cyclobutane moiety. The two primary products, hydroxy-dienes 20 and 25, result from the cycloreversion of the cyclobutane moiety. The cyclopentanol 21 - 24 are secondary products formed by intramolecular 'ene' reaction of hydroxy-diene 20 while aldehyde 26 is formed from diene 25 via two 'ene' reaction processes.

Pyrolysis of cis-verbanone 27 results in the formation of dienes 29 and 32. The absence of 28 can be rationalized if it is assumed that the cleavage of the cyclobutane ring occurs via the 1,4-biradical intermediates a and b (Scheme 2). The cleavage of the second C-C bond will occur most readily when the radical orbitals of the 1,4-biradical are eclipsed with this bond. For the 1,4-biradical a, the carbon atoms adjacent to the secondary radical are sp³-hybridized and the species can assume a conformation where the radical orbitals approach a geometry with overlap of the C(5),C(7) bond. The alternative biradical b has a carbonyl adjacent to the radical orbital which imposes an additional conformational constraint and reduces overlap of the radical orbital with the C(1),C(7) bond allowing the alternative route to 31 to compete with fragmentation.

The intermediacy of biradicals is attractive in rationalizing the pyrolysis of pinanes¹⁰. The general acceptance of this hypothesis may be traced to its versatility and consistency with experimental data. However, the evidence for the intermediacy of a 1,4-biradical is far from unequivocal.

From kinetic studies, the thermal decomposition of substituted cyclobutanes is homogenous and first order¹¹. Activation energies



Scheme 2

range from 51 kcal mole⁻¹ (log A = 14.61 sec⁻¹) for the formation of isoprene and ethylene from isopropenylcyclobutane ³⁸ to 65.2 kcal mole⁻¹ (log A = 16.31) for formation of isobutylene from 1,1,3,3-tetramethylcyclobutane ⁴⁰¹². The values of the Arrhenius parameters and also the rates of decomposition relative to cyclobutane ³⁴ at 450°C, of compounds studied to date are given in Table 1. The relative rate constants which vary only slightly cannot be directly collated with differences in Arrhenius parameters, which, themselves have relatively large errors

TABLE 1

Arrhenius parameters and relative rates for alkylcyclobutane decomposition

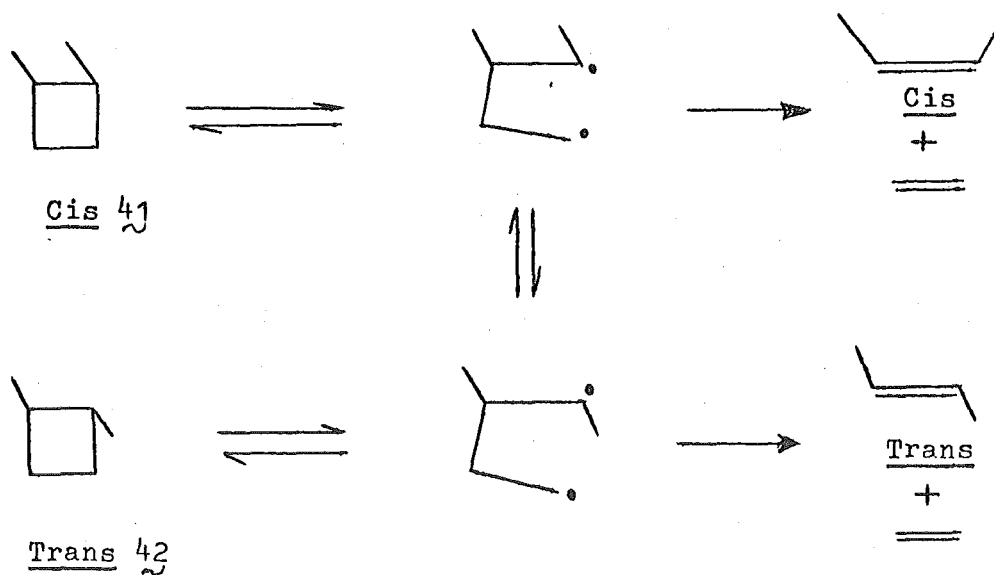
<u>Compound</u>	<u>log A</u>	<u>E_a (kcal mole⁻¹)</u>	<u>Relative rate at 450°</u>	<u>Reference</u>
34	15.62	62.5	1.00	13,14
35	15.38	61.2	1.46	15
36	15.56	62.0	1.26	16
37	15.53	61.6	1.56	17
38	15.63	62.6	0.98	18
39	15.68	61.0	3.34	11
40	16.31	65.2	0.73	11
41	15.68	60.8		19
42	15.67	62.0		19

associated with them. However, O'Neal and Benson²⁰ have shown that the biradical model²¹ is capable of accounting semi-quantitatively for all the experimental observations. From group additivity estimates and parameters obtained by consideration of the experimental results for cis- and trans-1,2-dimethylcyclobutane, 41 and 42, they are able to predict Arrhenius parameters for the thermal decomposition of other alkylcyclobutanes. The agreement between estimated and experimental values seems to be good. This agreement cannot, however, be taken as unambiguous evidence in favour of the diradical mechanism, and the relative rates of decomposition of monoalkylcyclobutanes (35 - 38) cannot be accurately predicted in this manner.

A biradical intermediate is thought to be formed by a concerted stretching and twisting of the reactant cyclobutane. This will bring the substituents on C(1) and C(3) into close proximity. The distortions of the reactant in going to the biradical are, however, complex. The effect of substituents on the activation energy will depend on three factors: (a) the destabilization of the reactant due to steric interactions of the incipient biradical by the substituents, (b) the stabilization of the incipient biradical by the substituents (c), the destabilization of the transition state by 1,3 interactions. The rate of decomposition of 1,1,3,3-tetramethylcyclobutane 40 is only one quarter of the rate of 1,1-dimethylcyclobutane 41 and this is suggested by Cocks and Frey¹¹, to be due to the interaction between the substituents in the C(1) and C(3) carbon atoms in the transition state.

The configuration of substituents on the cyclobutane influences reactivity; trans-1,2-dimethylcyclobutane 42 reacts to give propene more slowly (Δ Act. Energy = 1.2 kcal) than the

cis- isomer 41¹⁹. Benson¹⁴ suggests that the minor reaction pathway to give ethylene and but-2-ene goes via a biradical which has a life-time sufficient to allow rotation about the C-C bond (Scheme 3). The loss of stereochemical integrity i.e., trans-1,2-dimethylcyclobutane 42 gives 89% trans-butene and cis-1,2-dimethylcyclobutane 41 gives 64% cis-butene, can be accounted

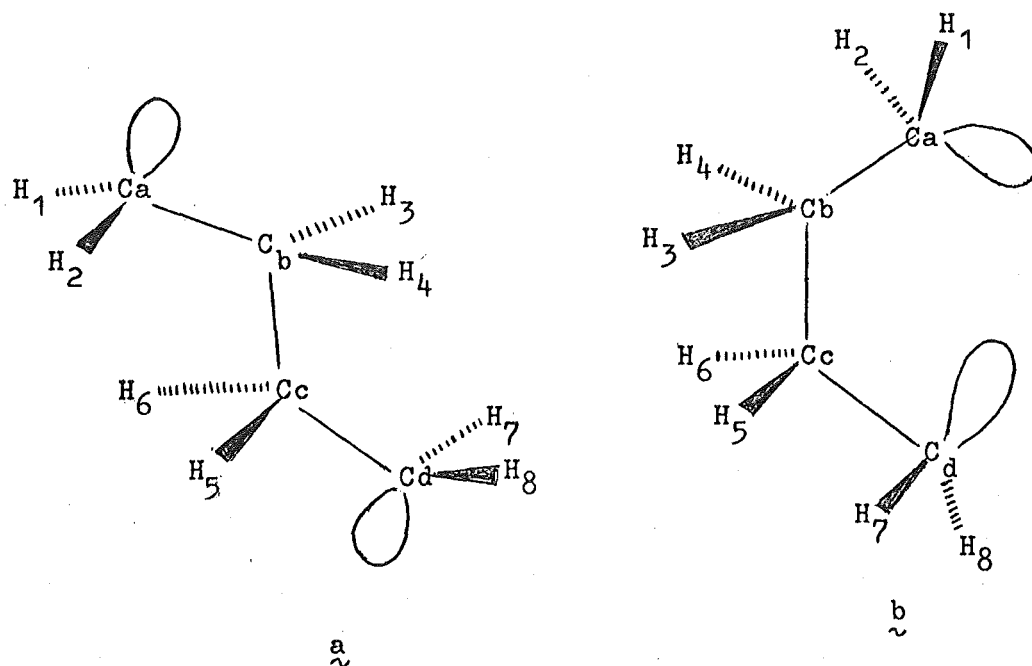


Scheme 3

for by this mechanism if the rate of bond rotation of the diradical is comparable with the rate of fragmentation of the biradical.

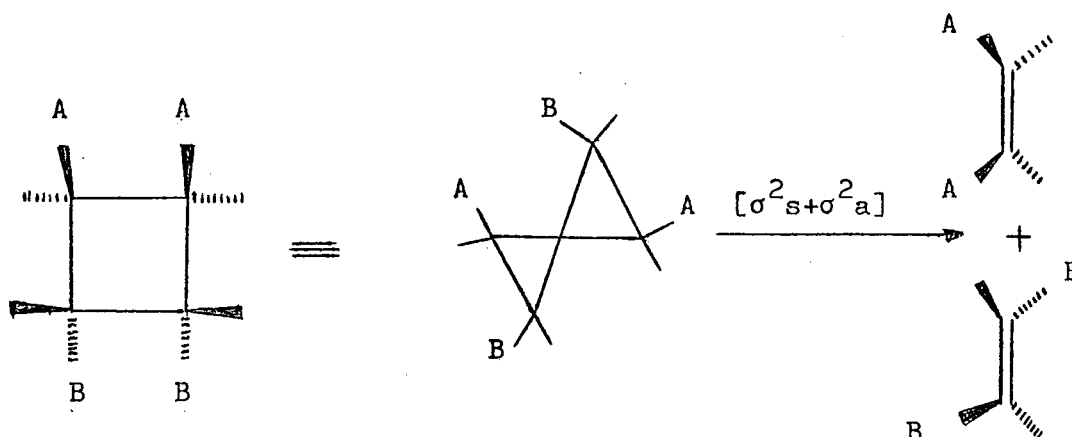
Recently, Dewar et al²² studied the fragmentation of cyclobutane 34 in detail using a MINDO/3 semiempirical SCF MO method and have calculated that fragmentation via a 1,4-biradical was the lowest energy pathway. The potential surface is divided by a ridge into a "two-valley" structure corresponding to biradical intermediates. The workers show that in the vicinity of

the transition state the system exists as one of two biradicaloid structures a and b. The calculated overall activation energy



for conversion of the cyclobutane to ethylene (62 kcal/mole) agrees well with the experimental value (62.5 kcal/mole¹⁴).

The alternative mechanism for the thermal cleavage of cyclobutanes which has received less support is the concerted mechanism which involves a symmetrical stretching of the two (opposite) carbon-carbon bonds in the ring to yield the olefin in one step. (i.e. a $[\sigma^2_s + \sigma^2_s]$ process). Until recently this concerted process was considered energetically unfavourable and from symmetry arguments is a forbidden reaction. The symmetry allowed concerted process $[\sigma^2_s + \sigma^2_a]$ would involve a very twisted transition state and would result in inversion at one of the ring carbon atoms (Scheme 4).



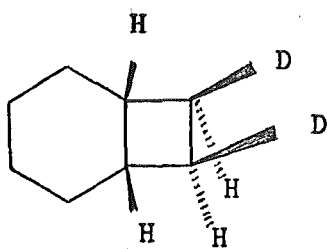
Scheme 4

This allowed concerted process could, however, account for some of the reaction products produced in cyclobutane pyrolysis.

Thermal decomposition of trans-6,7-dimethylbicyclo[3,2,0]-heptane ⁴⁴ yields but-2-ene with 75% retention of configuration and the cis-(exo)-isomer gives approximately equimolar amounts of the two but-2-ene isomers ²³. The workers claim that the evidence is strongly in favour of a biradical intermediate, but they suggest that the biradical is produced by a twisting of the cyclobutane ring.

Pyrolysis of 7,8-cis-exo-dideuterio-cis-bicyclo[4,2,0]-octane ⁴⁶, produced 1,2-dideuterioethylene which was $62 \pm 3\%$ trans ²⁴. This result demonstrates that a predominant portion of the reaction occurs in a stereochemical sense incompatible with both the biradical hypothesis or a completely concerted elimination of ethylene.

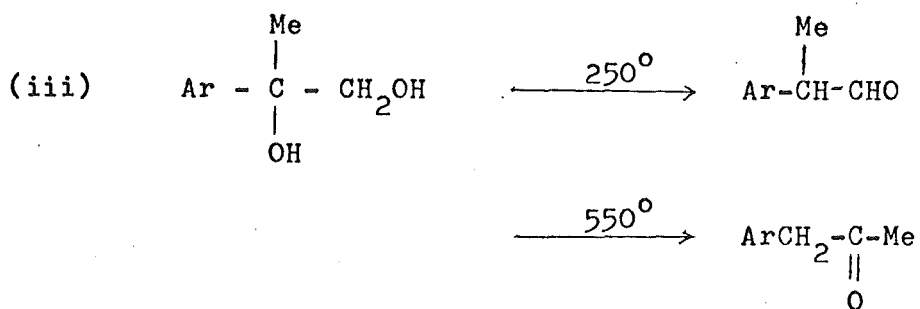
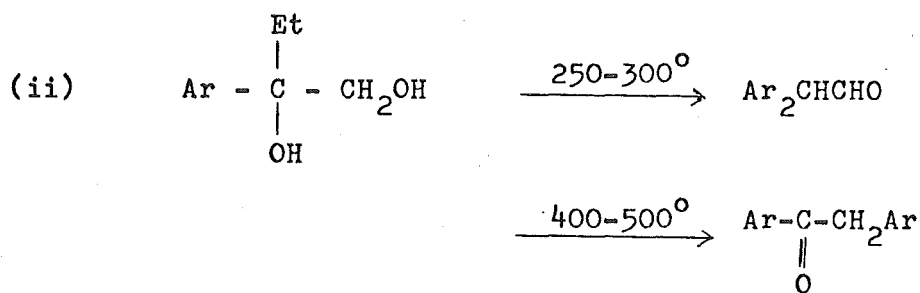
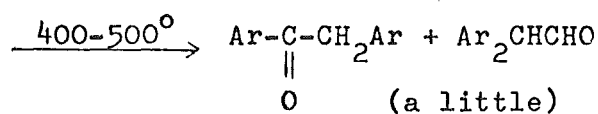
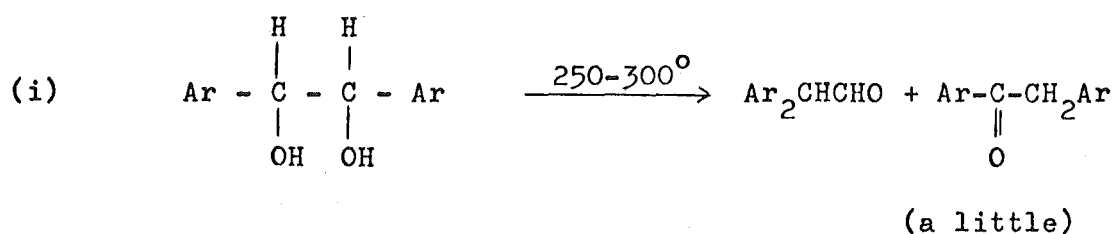
While many scientists favour the intermediacy of a 1,4-biradical in the thermal cleavage of cyclobutane and its

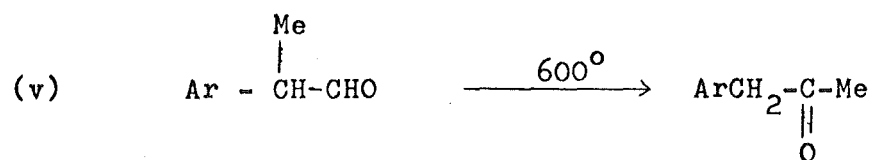
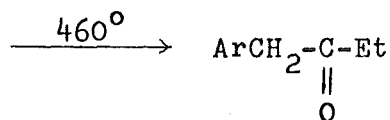
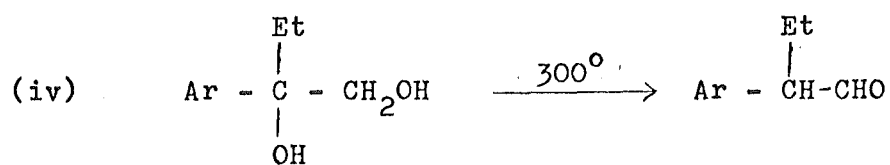
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derivatives, the experimental results in this area are in apparent conflict. The present work was directed to investigating the effect of substituents at C(1) and C(3) on the thermal fragmentation of cyclobutanes and extending knowledge of pinane thermolysis by a study of some diols and epoxide derivatives.

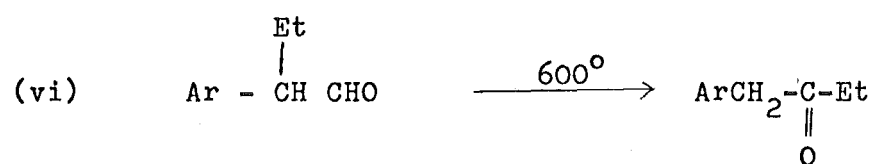
DISCUSSION

Despite extensive literature on the thermolysis of pinanes and substituted pinanes, there has been very little work done on the pyrolysis of pinane diols and epoxides. The dehydration of aryl diols has been studied by Ramart-Lucas and Salmon-Legagneur²⁵ in the early 1930's. The diol vapour was passed over heated 'infusorial earth' and at 200 - 300°C gave aldehydes which when heated at higher temperatures (300 - 600°C) isomerized to ketones. (Scheme 5).





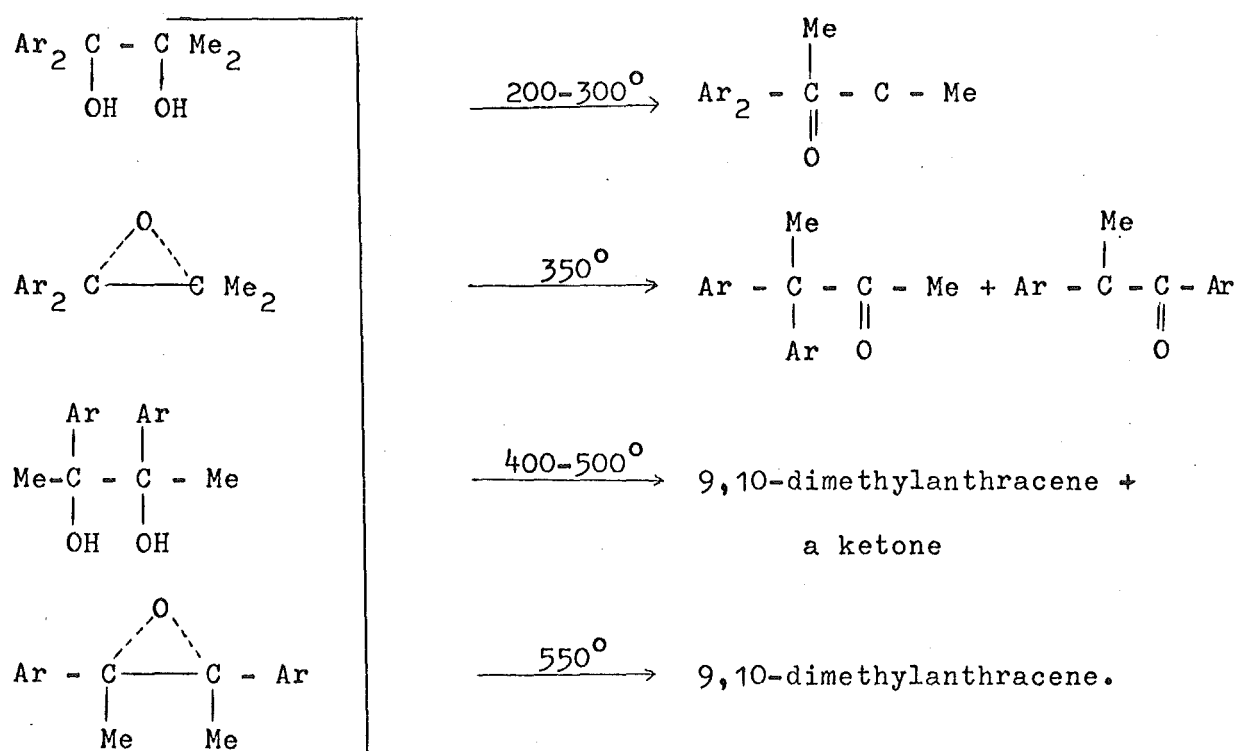
(partially rearranged)



(partially rearranged)

Scheme 5

They reported²⁶ that the thermolysis of two aryl diols gave the same products as obtained from the corresponding epoxides and their results are shown in (Scheme 6).

Scheme 6

The workers conclude that the formation of products depends less on the structure of the original isomers than on the temperature of transformation.

The present work deals with the pyrolysis of some pinane diols, namely, 10 β -pinane-2,3 α -diol 47 and 10 β -pinane-2,10-diol 48 and their corresponding epoxides.

10 β -Pinane-2,3 α -diol 48 was prepared by the oxidation of α -pinene with potassium permanganate²⁷. The diol was pyrolysed in the temperature range 450° - 600°C with an injection rate of 250 μ l/min and a carrier gas flow rate of 15 mls/min, to give a crude product (ca 90%), shown by g.l.c. to contain more than thirteen compounds. In addition to the starting material, two main products were isolated by preparative gas liquid chromatography and identified as 2,2,3-trimethyl cyclopent-3-ene-1-acetaldehyde 49 and 10 α -pinan-3-one 50. (Table 2.)

The infrared spectrum of 2,2,3-trimethylcyclopent-3-ene-1-acetaldehyde 49 showed absorption due to aldehyde group (ν_{\max} 1725, 2750 cm^{-1}). The n.m.r. spectrum exhibited two methyl singlets centered at δ 0.80 and 1.00, and the vinyl methyl appeared at δ 1.65. The olefinic proton appeared at δ 5.29 ($W_{h/2}$ = 6 Hz) and the aldehyde proton at δ 9.81 as a triplet (J = 2 Hz). The n.m.r. spectrum of 49 was identical to that of an authentic sample²⁸.

The infrared spectrum of 10 α -pinan-3-one 50 showed a ketone (ν_{\max} 1710 cm^{-1}) and the n.m.r. spectrum exhibited three methyl signals, namely, the C(9) methyl at δ 0.92, the C(8) methyl at 1.37 and the C(10) α -methyl which appeared as a doublet centered at δ 1.10, J = 7 Hz. The n.m.r. spectra was identical to an authentic sample²⁸.

Table 2

Yields (%) of products from pyrolysis of 10 β -pinane-2,3 α -
diol 48

	<u>Temperature</u>		
	<u>450°</u>	<u>500°</u>	<u>600°</u>
Low boiling compounds	15	15	25
Unknown 1	5	10	13
2,2,3-trimethylcyclopent-3-ene			
-1-acetaldehyde 49	18	20	25
10 α -pinan-3-one 50	20	25	27
Others	17	7	10

A minor product of pyrolysis which represented from 5 - 13% yield was isolated but could not be identified. ν_{\max} 3500, 3000, 2750, 1720, 1700 cm^{-1} . n.m.r. δ 0.88 (3 H), 2.40 (6 H). It appears that the product could be a mixture of two compounds which do not separate on g.l.c.

α -Pinene oxide 51 has been pyrolysed in an iron pipe at 260 - 350°C and is reported to give a useful perfumery compound, trans-carveol 52 in 10 - 15% yield, pinocamphone 50, 11 - 57% and starting material 79 - 25%²⁹. More recently³⁰ pyrolysis of the epimeric epoxide, 2,3-epoxy-10 α -pinane 53 under reduced pressure was shown to give a mixture of p-cymene 54, 2,2,3-trimethyl cyclopent-3-ene-1-acetaldehyde 49, cis-pinocarveol 55 and cis-carveol 56. In the present study pyrolysis of 2,3-epoxy-10 β -pinane 51 was similar to pyrolysis of 10 β -pinane-2,3 α -diol 48. The two major products were isolated by preparative g.l.c. and identified as 2,2,3-trimethyl cyclopent-3-ene-1-acetaldehyde 49 and 10 α -pinan-3-one 50. (Table 3). In this study, cis- and trans-carveol (52 and 56), p-cymene 54 and cis-pinocarveol 55 could not be isolated and therefore if present, are products formed in low yield (<5%).

10 β -Pinane-2,10-diol 47 was prepared by the oxidation of β -pinene with potassium permanganate in the presence of magnesium sulphate. The identity of the diol follows from the infrared (ν_{\max} 3280 cm^{-1}) and the n.m.r. spectrum which shows the (C10) H_2 -OH as a singlet centered at δ 3.52. Hydroxylation of β -pinene occurs from the least hindered α -face and the stereochemistry at C(2) was confirmed from the chemical shift of the C(8) methyl at δ 1.27⁶.

The diol was pyrolysed at 500 - 600°C with an injection rate

Table 3Yields (%) of products from pyrolysis of 2,3-epoxy-10 β -pinane 51

	<u>Temperature</u>	
	<u>500°</u>	<u>600°</u>
Low boiling compounds	10	12
2,2,3-trimethylcyclopent-3-ene-		
1-acetaldehyde 49	36	40
10 α -pinan-3-one 50	38	37
Others	16	11

of 250 $\mu\text{l}/\text{min}$ and a carrier gas flow of 15 mls/min . The crude pyrolysate (ca 90%) was shown by g.l.c. to contain more than sixteen compounds. Three of the four main products were isolated by preparative g.l.c. and identified as 10 α -pinan-10-al 58, myrtenol 59, and perillyl alcohol 60. (Table 4).

The identity of 10 α -pinan-10-al follows from the infrared spectra (ν_{max} 1720, 2700 cm^{-1}) which shows the presence of an aldehyde moiety and from the n.m.r. spectrum. The C(9) methyl appeared as a singlet centered at δ 0.88 and the C(8) methyl at 1.25. The aldehyde proton appeared as a doublet centered at 9.60 ($J = 3$ Hz). The structure was further established by its identity to an authentic sample²⁷.

The infrared spectrum of myrtenol 59 had a broad hydroxyl band (ν_{max} 3200 - 3600 cm^{-1}). In the n.m.r. spectra, the C(8) and C(9) methyl groups appeared at δ 1.30 and 0.83 respectively. The C(10) methylene protons appeared as a singlet δ 4.0 ($W_{h/2} = 4$ Hz) and the olefinic proton was centered at 5.43 ($W_{h/2} = 7$ Hz). The n.m.r. spectrum was identical to that of an authentic sample of myrtenol 59.

The infrared spectrum of perillyl alcohol 60 gave a wide hydroxyl band in the infrared spectrum (ν_{max} 3200 - 3600 cm^{-1}). The n.m.r. spectrum exhibited a vinyl methyl peak at δ 1.73 and a broad olefinic methylene peak centered at δ 4.73 ($W_{h/2} = 4$ Hz). The C(10) methylene protons appeared at δ 4.0 ($W_{h/2} = 4$ Hz) and the C(3) olefinic proton was centered at δ 5.75 ($W_{h/2} = 8$ Hz). The n.m.r. spectrum was identical with that of an authentic sample of perillyl alcohol 60³¹.

The pyrolysis of 2,10-epoxy-10 β -pinane 57 was similar to pyrolysis of 10 β -pinane 2,10-diol 47 but the yields of products

Table 4

Yields (%) of products from pyrolysis of 10 β -pinane-2,10-
diol 47

	<u>Temperature</u>	
	<u>500°</u>	<u>600°</u>
Low boiling compounds	10	13
Unknown 1	10	12
10 α -Pinan-10-al 58 ~	31	33
Myrtenol 59 ~	15	10
Perillyl Alcohol 60 ~	20	21
Others	14	11

differed. (Table 5), The major product of pyrolysis was isolated by preparative gas liquid chromatography and identified as 10 α -pinan-10-al 58, by comparison of the n.m.r. and infrared spectra with that of authentic samples. The two minor products were shown to be myrtenol 59 and perillyl alcohol 60 by g.l.c.

cis- Myrtanol 83 prepared by E. Danstedt was pyrolysed at 500 - 600°C with an injection rate of 250 μ l/min and a carrier gas flow of 15 mls/min. The crude product (ca 95%) was shown by g.l.c. to contain more than four compounds. In addition to the starting material one other product was isolated and identified as 7-methylocta-1,6-diene-3-carbinol 84. (Table 6).

7-Methylocta-1,6-diene-3-carbinol 84 had an infrared absorption (ν_{max} 3400 cm^{-1}) due to the hydroxyl group. The vinyl methyls were deshielded and appeared at δ 1.60 and 1.67 in the n.m.r. spectrum. The four olefinic protons appeared as a multiplet δ 4.9 - 5.5. The $\text{CH}_2\text{-OH}$ protons appeared as a multiplet centered at δ 3.50. The accurate mass of the parent ion was measured as 154.136145 g. mol $^{-1}$. $\text{C}_{10}\text{H}_{18}\text{O}$ requires 154.135758 g. mol $^{-1}$.

The 'Lewis' acid catalysed rearrangement of 2,3-epoxy-10 β -pinane 51 is reported to give 2,2,3-trimethylcyclopent-3-ene-1-acetaldehyde^{32,33} 49 and 10 α -pinan-3-ene³⁴ 50. Lewis and Hedrick³⁵ have studied this reaction carefully and found that using zinc bromide the reaction yielded 96% pure 2,2,3-trimethylcyclopent-3-en-1-acetaldehyde 49 and they could not isolate the ketone 50. The thermal rearrangement of 10 β -pinane-2,3 α -diol sulphites (85 and 86) in Carbowax at 200°C gave a product consisting of a 98:2 mixture of 10 α -pinan-3-one 50 and 2,2,3-

Table 5

Yields (%) of products from pyrolysis of 2,10-epoxy-10 β -
pinane 57

	<u>Temperature</u>	
	<u>500°</u>	<u>600°</u>
Low boiling compounds	5	7
Unknown 1	5	6
10 α -Pinan-10-al 58 ~	70	71
Myrtenol 59 ~	3	2
Perillyl Alcohol 60 ~	9	8
Others	8	6

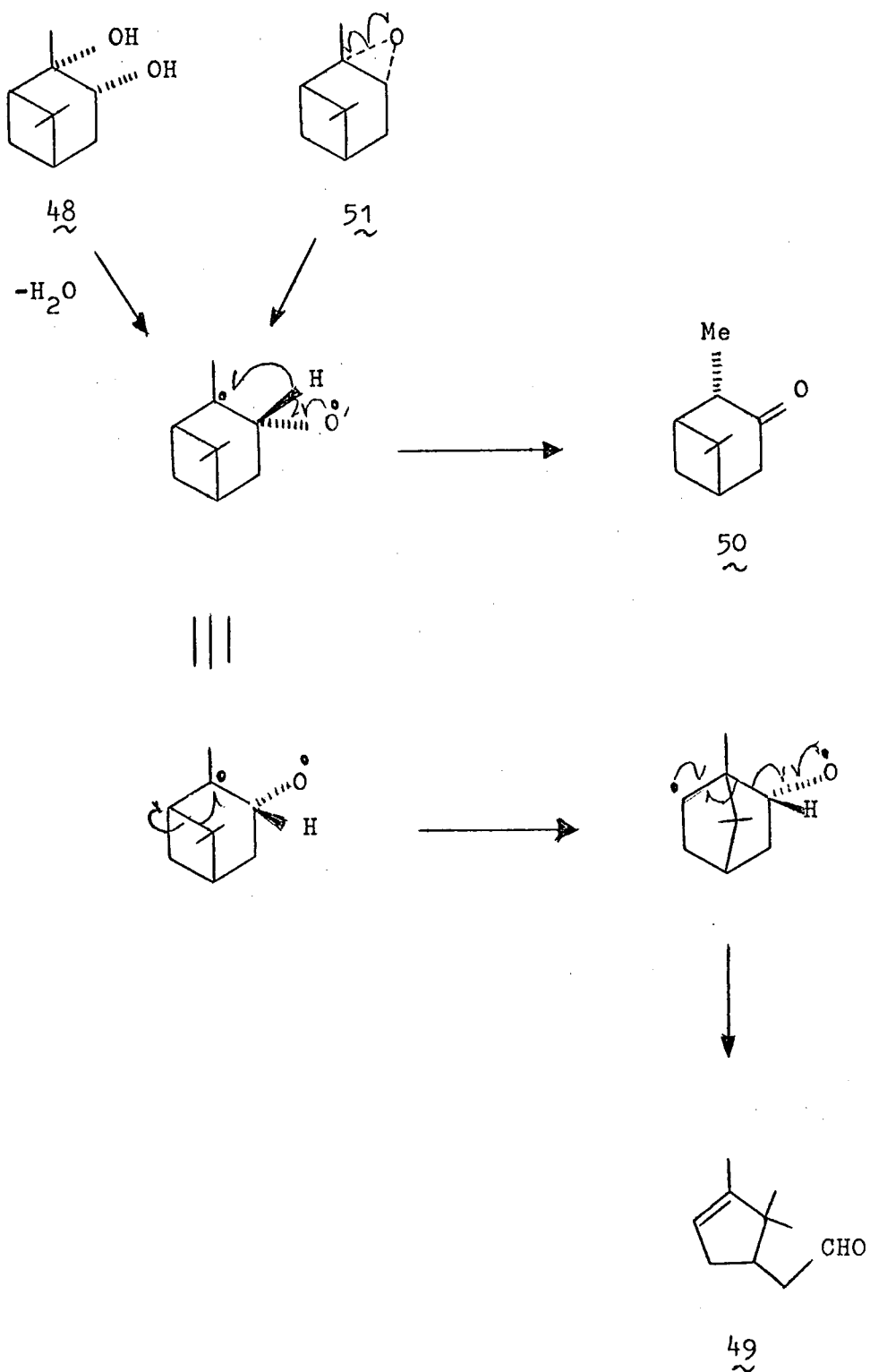
Table 6Yields (%) of products from pyrolysis of cis- Myrtanol 83

	<u>Temperature</u>	
	<u>500°</u>	<u>600°</u>
Low boiling compounds	3	8
7-Methylocta-1,6-diene-3-carbinol	7	48
Starting Material	88	35
Others	2	9

trimethylcyclopent-3-en-1-acetaldehyde 49. It seems probable that with the breaking of the (C2)-O bond, the cyclic sulphite would move to a slightly 'up' conformation in which the 3 β -hydrogen would be well placed for migration to the 2 β -position concerted with (C2)-O bond cleavage. In contrast to this mobility accommodated by the flexible cyclic sulphite ring system, the conformations energetically available to α -pinene oxide 51 during its 'Lewis' acid catalysed rearrangements are limited by the constraint imposed by the attachment of the leaving group directly to C(3).

However, in the thermal reaction of α -pinene oxide 51, the molecule will have greater conformational flexibility. Pyrolysis of α -pinene oxide 51 in iron pipe at 260 - 350°C is reported to give trans-carveol 52 (10 - 15%), 10 α -pinan-3-one 50 (11 - 57%) and starting material (79 - 25%). In our hands pyrolysis of α -pinene oxide at 500 and 600°C gave 2,2,3-trimethylcyclopent-3-en-1-acetaldehyde 49, (36, 40%) and 10 α -pinan-3-one 50, (38, 37%). These two products (49 and 50) were also found to be the main products from the pyrolysis of 10 β -pinane-2,3 α -diol 48. The g.l.c. of pyrolysate of the diol 48 and the epoxide 51 are comparable, and it appears that under thermal conditions, these compounds rearrange via a similar pathway. (Scheme 7).

2,10-Epoxy-10 β -pinane 57 on reaction with zinc halides gives pinan-10-al of undefined stereochemistry³⁶. Reaction with alumina is reported to give 10 α -pinan-10-al 58 and pin-2-en-10-ol 59. Boron trifluoride etherate rearrangement of 2,10-epoxy-10 β -pinane 57 gave in approximately 1:1 ratio the isomeric aldehydes, 10 α -pinan-10-al and 10 β -pinan-10-al²⁷. The

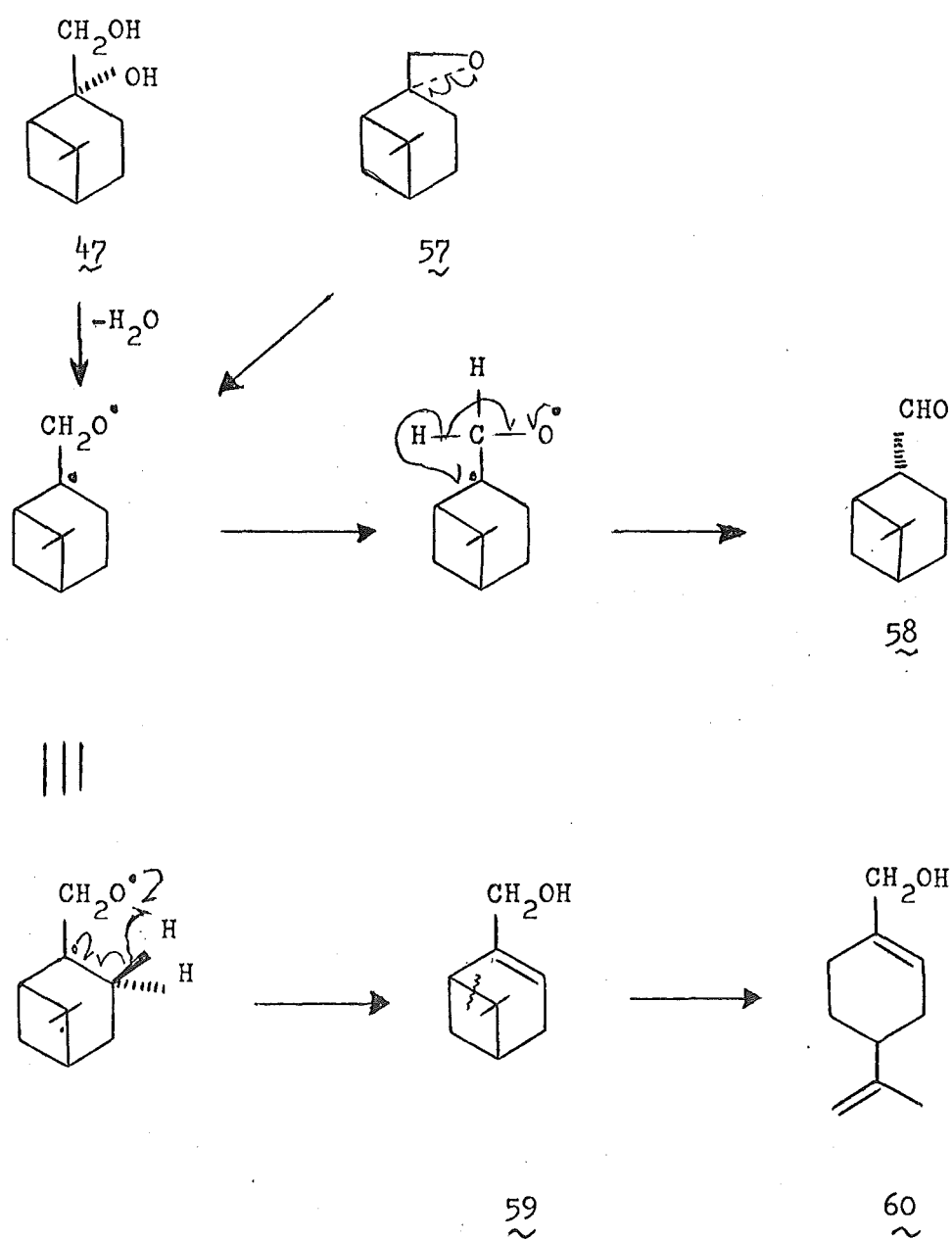


Scheme 7

significant formation of the thermodynamically less stable aldehyde, 10 β -pinan-10-al reflects the steric hindrance of the geminal dimethyl group to a β -face hydride shift. However, in the thermal rearrangement of β -pinene oxide 57 there is sufficient energy for the molecule to overcome this energy barrier and 10 α -pinan-10-al 58 is the major product. β -Pinene oxide on thermolysis at 500° and 600°C gave in addition to 10 α -pinan-10-al 58 (70, 71%), myrtenol 59 (3, 2%) and perillyl alcohol 60 (9, 8%). Myrtenol can be formed as shown in Scheme 8.

10 β -Pinan-2,10-diol cyclic sulphite 66 on refluxing in pyridine rearranged to give a 53:19:28 ratio of 10 β -pinan-10-al, 10 α -pinan-10-al 58 and pin-2-en-10-al 59²⁷. However, in the pyrolysis of 10 β -pinane-2,10-diol 47 at 500° and 600°C no 10 β -pinan-10-al could be isolated (Table 4). The g.l.c. of the pyrolysate of 10 β -pinan-2,10-diol 47 and 2,10-epoxy-10 β -pinane 57 are comparable and it seems probable that under thermal conditions the diol and epoxide give products via a similar pathway (Scheme 8).

The upsurge of interest in the pyrolysis of pinanes for industrial purposes has directed studies towards understanding the factors controlling the thermal rearrangement of pinane derivatives. Most of the products derived from pinane pyrolysis result from the cleavage of the pinane cyclobutane ring. The mechanism of cyclobutane fragmentation is not well understood and the results in this area are in apparent conflict. Thus there is a need for more fundamental knowledge concerning thermal cleavage of substituted cyclobutanes. This study concerns the pyrolysis of cyclobutanes which contain gem dimethyls at C(2) and substituents at C(1) and C(3).



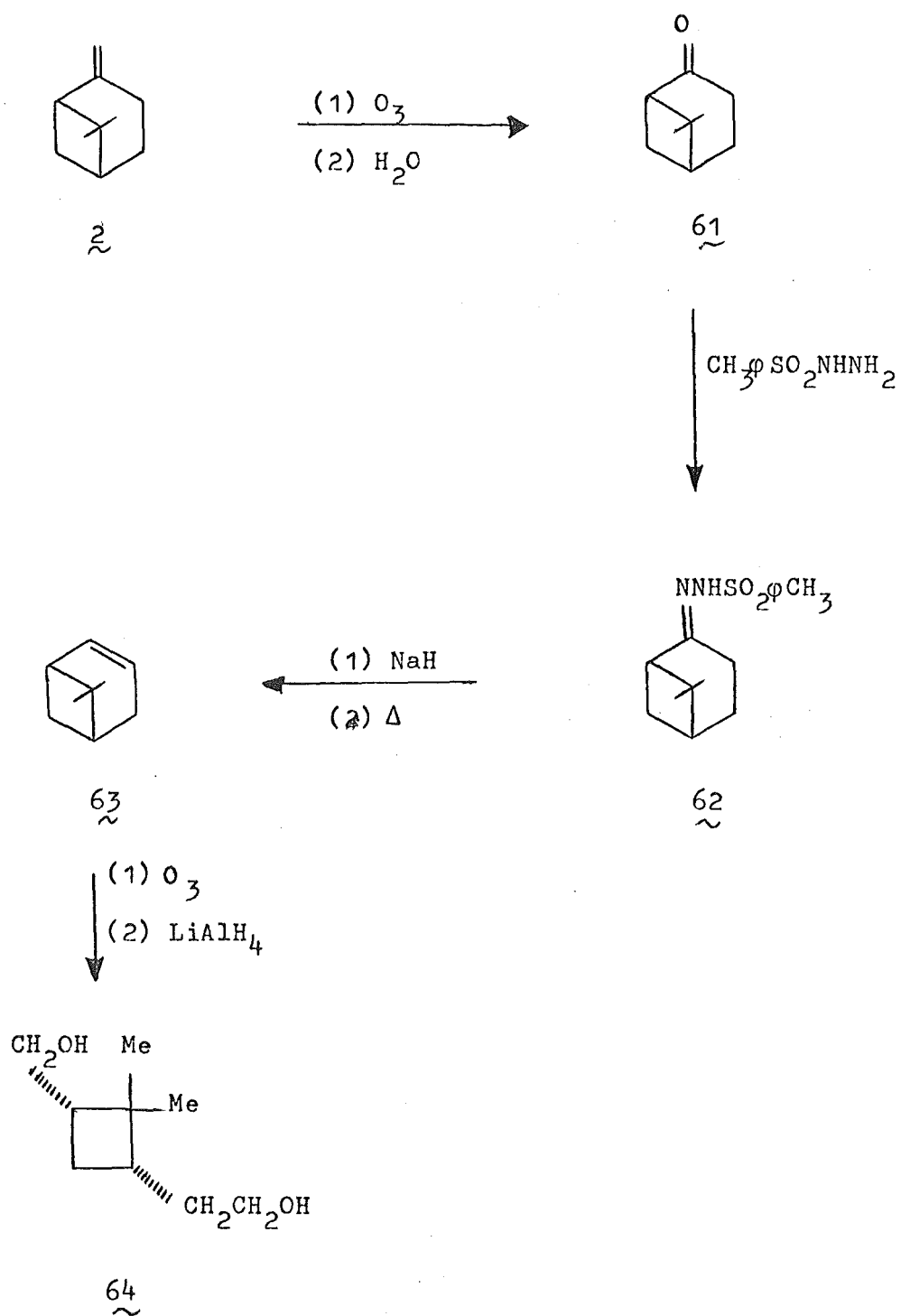
Scheme 8

The isomeric 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxy-methylcyclobutane 64 and 65 were prepared in two ways. The first by degradation of β -pinene as shown in Scheme 9. Ozonolysis of β -pinene gave in high yield nopinone 61 (ca 70% yield)³⁷ which was converted to its toluene-4-sulphonhydrazone derivative 62 by reaction with toluene-4-sulphonhydrazine catalysed by p-toluene sulphonic acid. The sodium salt of the hydrazone was prepared by the method of W. M. Jones³⁸. The hydrazone was dissolved in dry T.H.F. and one equivalent of sodium hydride (obtained as a 50% suspension in mineral oil) was added slowly with stirring. The resulting precipitate was filtered and dried in a vacuum dessicator.

Norpinene 63 was prepared by heating the sodium salt of the hydrazone to a temperature of 165°C. The decomposition has to be carried out on a small scale (ca 10 gm.) and if possible stirred otherwise exothermic decomposition to a black tar occurs. The products of decomposition were removed under reduced pressure and collected in a dry ice acetone trap. The crude product was purified by spinning band distillation.

Ozonides have been reported to be reduced directly to alcoholic products by reaction with sodium borohydride or lithium aluminium hydride^{39,40}. In addition to the desired products, anomalous products have been found in ozonolysis reactions^{41,42}. It has been emphasized by several groups of workers that the solvent plays an important part in the formation of products.

Norpinene 63 was dissolved in ether and ozone was bubbled through until the effluent gases gave a strong colouration with moist starch iodide paper. Three equivalents of lithium



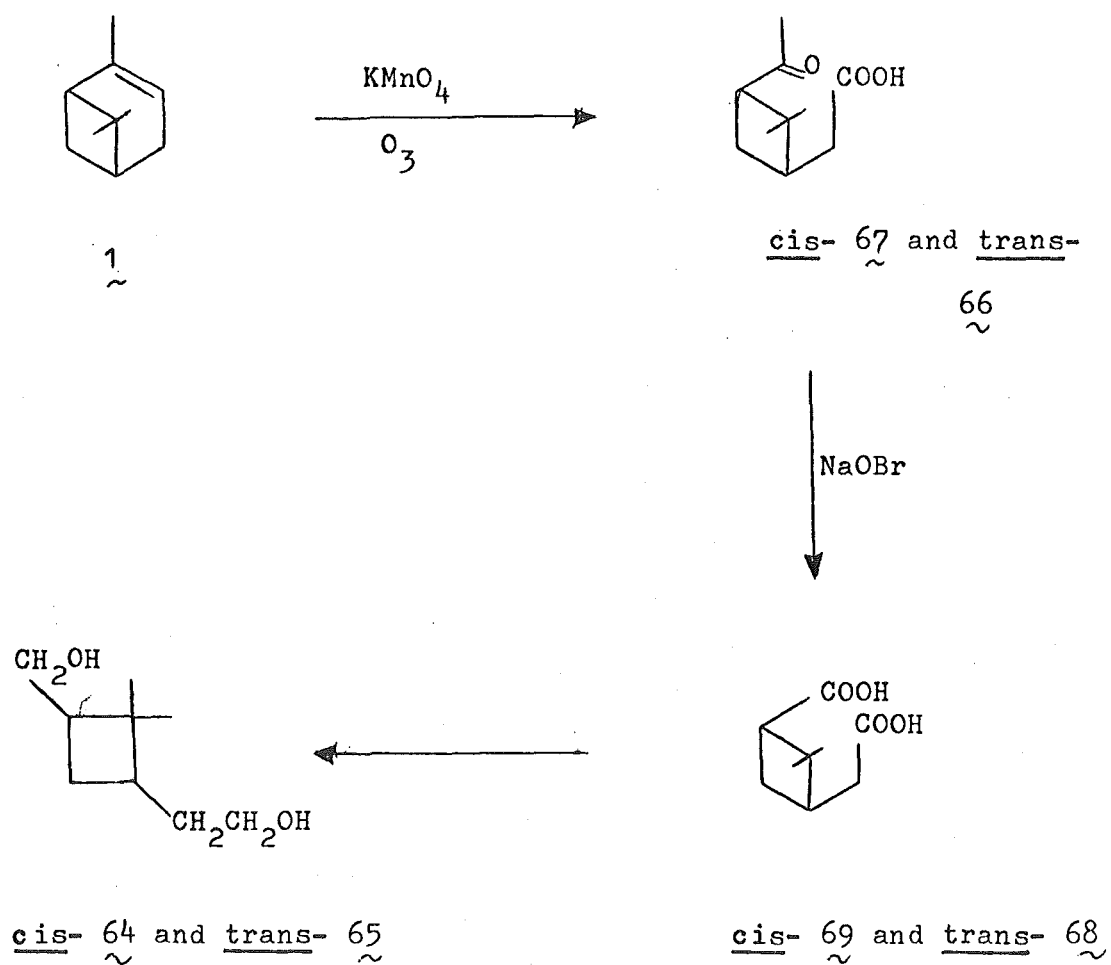
Scheme 9

aluminium hydride were slowly added to the ozonide with rapid stirring and the mixture was heated under reflux for two days. Even after this time no diol could be detected by t.l.c. and it was found necessary to add T.H.F., remove the ether and continue to heat under reflux for a further three days. The procedure afforded only 20 mg. of pure diol. Attempts to improve the yield of the diol from this reaction sequence proved unsuccessful.

The diols 64 and 65 were also prepared from α -pinene as shown in Scheme 10. The discovery that esters of pinic acid 68 and 69 have excellent lubricant⁴³ and plasticizer^{44,45} properties has stimulated interest in this compound and its precursor pinonic acid. Pinonic acid 66 and 67 is readily prepared by the oxidation of α -pinene with potassium permanganate or with ozone in suitable solvents. Further oxidation with hypochlorite or hypobromite gives pinic acid⁴⁶.

We prepared pinonic acid in ca 30% yield by these methods. The pinonic acid prepared was shown from the n.m.r. spectrum to be predominantly the cis- isomer as shown by methyl singlets centered at δ 0.90 and 1.37, acetyl, 2.1, and a 4 H multiplet (δ 2.0 - 3.0). (Lit. cit.⁴⁷ n.m.r. δ 0.90 (singlet, β -CH₃), 1.37 (singlet, α -CH₃)). cis- and trans- Pinic acid 68 and 69 were prepared in high yields (>75%) by the oxidation of pinonic acid by bromine in aqueous sodium hydroxide solution. The n.m.r. spectrum again indicated the predominance of the cis- isomer as shown by methyl singlets centered at δ 1.00 and 1.25, and a 6 H multiplet (δ 2.0 - 4.0). (Lit. cit.⁴⁷. δ 1.00 (singlet, β -CH₃), 1.25 (singlet, α -CH₃)).

The pinic acids 68 and 69 were reduced by lithium aluminium hydride in dry T.H.F. to give a mixture (68:32) of cis- and trans- 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclo-



Scheme 10

butane 64 and 65. The diol mixture did not resolve on t.l.c. but analytical g.l.c. showed both isomers and also indicated two other impurities. For pyrolysis purposes the diol was purified by preparative gas liquid chromatography on 10% Carbowax 20 M column. The retention time necessary to obtain any sort of separation was long (2 hrs.) and only small injections could be made (25 μ l). Fractions of the isomers in varying ratio (75:25, 72:28, 67:33, 65:35, 71:29; cis:trans) were obtained in this way. The diols 64 and 65 were identified from the infrared absorptions at 3350, 2975, 1465, 1350, 1050 cm^{-1} and the n.m.r. spectrum. The gem-dimethyls of the cis- isomer appeared as singlets centered at δ 0.95 and 1.11 and that of the trans- isomer at δ 1.00 and 1.05. The $-\text{CH}_2\text{-OH}$ signals appeared as multiplets at δ 3.50 ($W_{h/2} = 18$ Hz). The accurate mass of the parent ion of a (75:25; cis:trans) mixture (158.131140 g. mol^{-1}) is consistent with the assigned structure. $\text{C}_9\text{H}_{18}\text{O}_2$ requires 158.130668 g. mol^{-1} .

In an attempt to prepare cis- and trans- 2,2-dimethyl-1-ethyl-3-methylcyclobutane 81 and 82, the ditosylate of the diols (64 and 65) was required. Reaction of the cis- and trans- diols 64 and 65 with p-toluenesulphonyl chloride in pyridine gave a reaction product which showed three spots on a t.l.c. plate. The major component was identified as a mixture of the 2,2-dimethyl-1-(2-hydroxyethyl)-3-tosyloxymethylcyclobutanes 74 and 75 (60:30; cis:trans). The identity of the isomeric compounds follows from the infrared ($\nu_{\text{max}} 3450 \text{ cm}^{-1}$) and n.m.r. spectrum. The cis- compound exhibited (gem-dimethyl) three proton singlets centered at δ 0.83 and 1.02, and an aromatic methyl at δ 2.42. The $\text{CH}_2\text{-OH}$ was a triplet centered at δ 3.39 and the $\text{CH}_2\text{-OTs}$ was

deshielded (δ 3.94, $J = 7$ Hz) relative to the corresponding $\text{CH}_2\text{-OH}$ in the starting diol. The aromatic protons appeared as an AB quartet centered at δ 7.50. The gem-dimethyls of the trans- compound were centered at δ 0.93 and 0.98.

The required 2,2-dimethyl-1-(2-tosyloxyethyl)-3-tosyloxy-methylcyclobutane was formed only in low yield and exhibited methyl singlets between (δ 0.72 - 1.10) and a aromatic methyl singlet centered at δ 2.42 with aromatic protons as an AB quartet centered at δ 7.55 ($J_{\text{AB}} = 9$ Hz, $\Delta\delta = 0.20$). A four proton multiplet ($W_{\text{h}/2} = 10$ Hz) was centered at δ 3.90. The only other products isolated were the isomeric dichloro-compounds 77 and 78 which showed cis- methyl singlets centered at δ 0.99 and 1.15 and trans- methyl singlet at δ 1.09. A four proton multiplet was centered at δ 3.4 ($W_{\text{h}/2} = 7$ Hz). Elemental analysis was consistent with the assigned structures.

Repeated attempts to prepare the ditosylate in higher yeild, all failed and the preparation of 2,2-dimethyl-1-ethyl-3-methylcyclobutane (81 and 82) was therefore abandoned.

The diol mixture 64 and 65 (68:32), was methylated with diazomethane solution in the presence of catalytic amounts of fluroboric acid. It was found that the reaction requires more catalyst (ca 5x) than is generally recommended⁴². The crude mixture of (78:22, cis:trans) -2,2-dimethyl-1-(2-methoxyethyl)-3-methoxymethylcyclobutane 72 and 73 was isolated by dry column chromatography and purified by preparative gas liquid chromatography. The isomeric compounds 72 and 73 were identified from the infrared absorptions at 2920, 2850, 1390, 1360, 1110 cm^{-1} and the n.m.r. spectrum. The gem-dimethyls of the cis- compound 72 appeared as singlets centered at δ 0.90 and 1.05 and that of

the trans- compound at δ 0.97 and 1.02. The $-O-\underline{\text{CH}}_3$ signals appeared as a singlet centered at δ 3.21. The accurate mass of the parent ion of a (79:21; cis:trans) mixture of 72 and 73 is consistent with the assigned structure. For pyrolysis purposes, fractions varying in isomer ratio (93:7, 86:14, 79:21, 77:23, 58:42; cis:trans) were obtained by preparative gas liquid chromatography on 8 $\frac{1}{2}$ % E.G.A. column.

In the n.m.r. spectrum of pinanes, the chemical shift of the axial methyl ((C8)H₃) is relatively invariant with change of substituent at C(2), C(3) and C(4) but varies with substitution at C(7) — endo (Table 7). The proton resonance signal for (C8)H₃ is generally downfield (ca 1.20 ppm) of (C9)H₃ (equatorial methyl ca 0.85) which varies significantly with substitution on the six-membered ring and little with change of substituent at C(7). The data has led to the suggestion that a low field shift area of the puckered cyclobutane ring is located in the axial direction as shown in Fig. 1⁴⁹.

For a series of 1,3-disubstituted cyclobutane derivatives the chemical shift of the methyls have been shown to be remarkably dependent on the type of substituent and their configuration on the cyclobutane ring⁴⁷ (Table 8). A notable feature of the proton magnetic resonance spectrum of the cis-isomers is the deshielding of the axial methyl compared to the equatorial. This contrasts with the trans- isomers where the equatorial methyls are deshielded by the axial substituent. A similar dependence on configuration was observed for the 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutanes (64 and 65) and 2,2-dimethyl-1-(2-methoxyethyl)-3-methoxymethylcyclobutanes (72 and 73) (Table 9). This data is summarized in Table 10.

Chemical Shifts of Methyl Groups in Pinanes

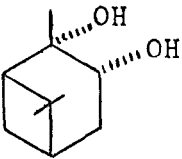
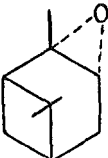
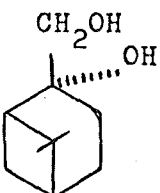
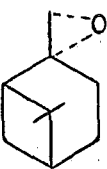
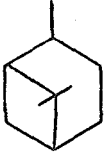
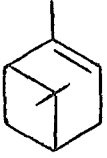
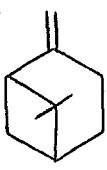
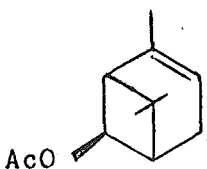
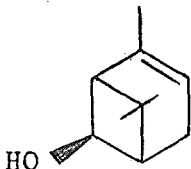
<u>Compound</u>	<u>Chemical Shift (δ)</u>			<u>Ref.</u>
	<u>C(8)</u>	<u>C(9)</u>	<u>C(10)</u>	
	1.23	0.93	1.26	50
	1.27	0.94	1.27	49
	1.27	0.93	3.52	6
	1.23	0.92	-	50
	1.20	1.02	1.01	49
	1.27	0.84	1.65	49
	1.23	0.72	-	49
	1.46	0.92	1.68	51
	1.56	0.89	1.66	51

Table 7

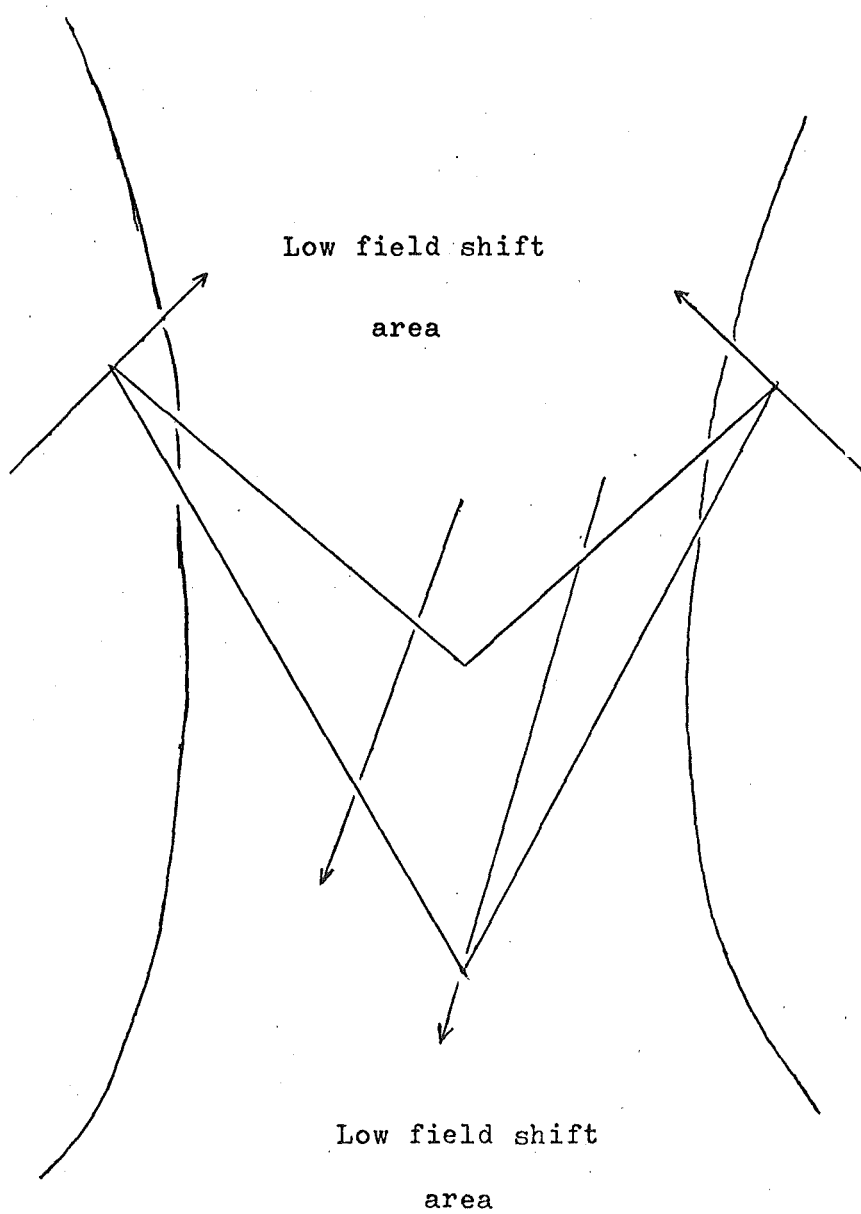
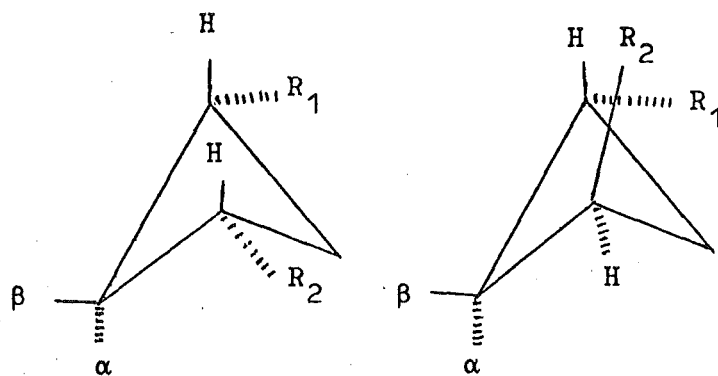


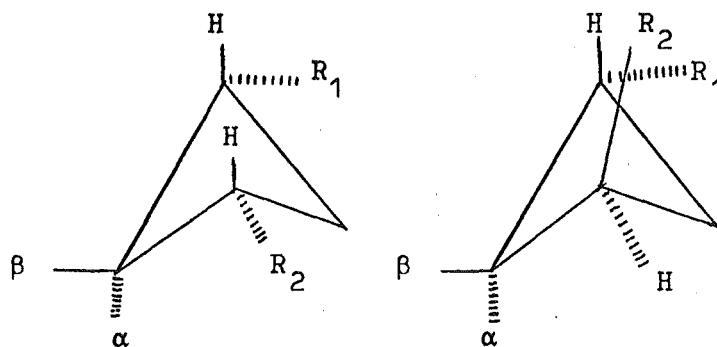
Fig. 1

Table 8N.M.R. data (Hz) for 1,3-disubstituted-2,2-dimethyl-cyclobutanes

<u>R₁</u>	<u>R₂</u>	<u>α</u>	<u>β</u>	<u>α</u>	<u>β</u>
CH ₂ CO ₂ Me	COMe	79	50	60	71
CO ₂ H	COMe	87	58	70	80
CH ₂ CO ₂ Me	CO ₂ Me	72	53	60	66
CH ₂ CO ₂ H	COMe	82	54		
CH ₂ CO ₂ H	CO ₂ H	74	61		

Table 9

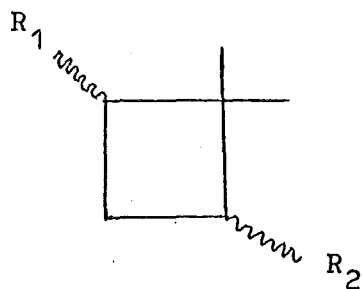
N.M.R. data (Hz) for 1,3-disubstituted-2,2-dimethylcyclo-
butanes



<u>R₁</u>	<u>R₂</u>	<u>α</u>	<u>β</u>	<u>α</u>	<u>β</u>
CH ₂ CH ₂ OH	CH ₂ OH	65	56	60	63
CH ₂ CH ₂ OMe	CH ₂ OMe	63	54	58	61
CH ₂ CH ₂ Cl	CH ₂ Cl	69	59	64	64
CH ₂ CH ₂ OH	CH ₂ OTs	62	50	56	59

Table 10

Substituent shift data for 2,2-dimethyl-1,3-disubstituted
cyclobutanes



<u>R₁</u>	<u>R₂</u>	<u>Δδ (trans-cis)</u> <u>pseudo axial CH₃</u>	<u>Δδ (trans-cis)</u> <u>pseudo eq. CH₃</u>	<u>Ref</u>
CH ₂ CO ₂ Me	COMe	-19	+21	47
CO ₂ H	COMe	-17	+22	47
CH ₂ CO ₂ Me	CO ₂ Me	-12	+13	47
CH ₂ CH ₂ OH	CH ₂ OH	-5	+7	*
CH ₂ CH ₂ OMe	CH ₂ OMe	-5	+6	*

* Present work.

It can be seen clearly that in the trans- case the equatorial methyl is considerably deshielded whereas in the cis- the axial methyl is more dishielded.

To confirm the assignments of the methyl signals, Eu(fod)₃ studies were carried out on 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutane (64 and 65), 2,2-dimethyl-1-(2-methoxyethyl)-3-methoxymethylcyclobutane (72 and 73) and cis- pinic acid (69). In particular, methyls assigned as equatorial of the cis- compounds (64, 72 and 69) experienced the greatest shift on addition of Eu(fod)₃ (Fig. 2, 3, and 4). This was not expected since the equatorial CH₂OR group of the cis- compounds is in closer proximity to the axial methyls. However, it is unlikely that the assignments can be reversed since the substituent shift data would become inconsistent.

It was not possible to obtain pure samples of the cis- and trans- isomers of 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutane (64 and 65) and 2,2-dimethyl-1-(2-methoxyethyl)-3-methoxymethylcyclobutane (72 and 73) for the pyrolysis studies since they could not be sufficiently resolved by preparative g.l.c. even with retention times as long as two hours. We could however obtain fractions containing different ratios of the cis- and trans- isomers.

Different ratios of cis- and trans- 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutane 64 and 65 were pyrolysed at 650°C with an injection rate of 250 µl/min and a carrier gas flow of 15 mls/min. The pyrolysate (ca 70%) was shown by g.l.c. to contain a very high percentage (ca 50%) of low boilers and two main products in addition to the starting material. The two products were isolated by preparative gas liquid chromat-

Fig. 2 Graph of $[\text{Eu}(\text{Fod})_3]$ v's chemical shift of cis- and trans- 2,2-dimethyl-1-(2-hydroxy-ethyl)-3-hydroxymethylcyclobutane (64 and 65)

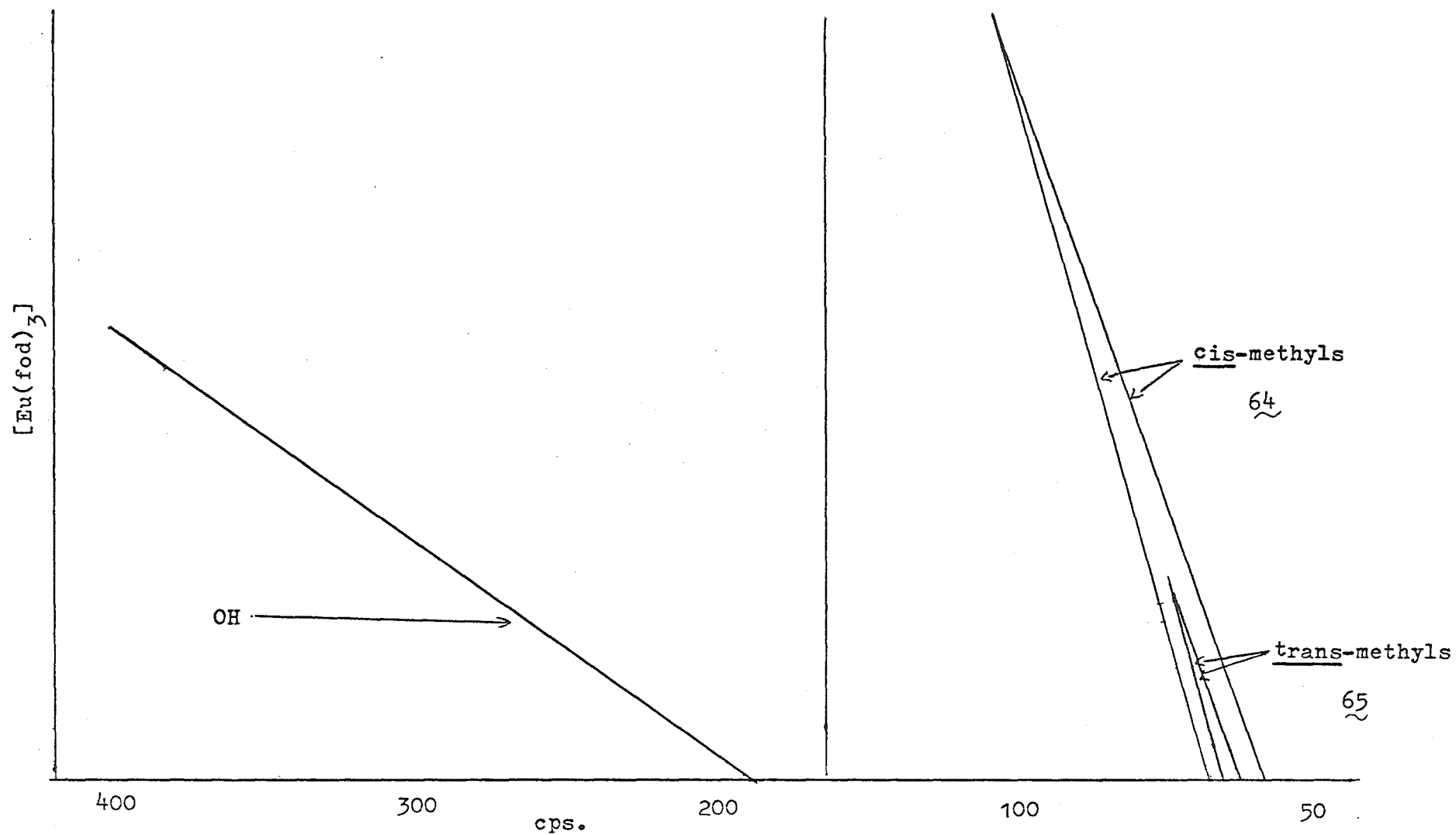


Fig. 3 Graph of $[\text{Eu}(\text{fod})_3]$ v's chemical shift of cis- and trans- 2,2-dimethyl-1-(2-methoxyethyl)-3-methoxymethylcyclobutane (72 and 73)

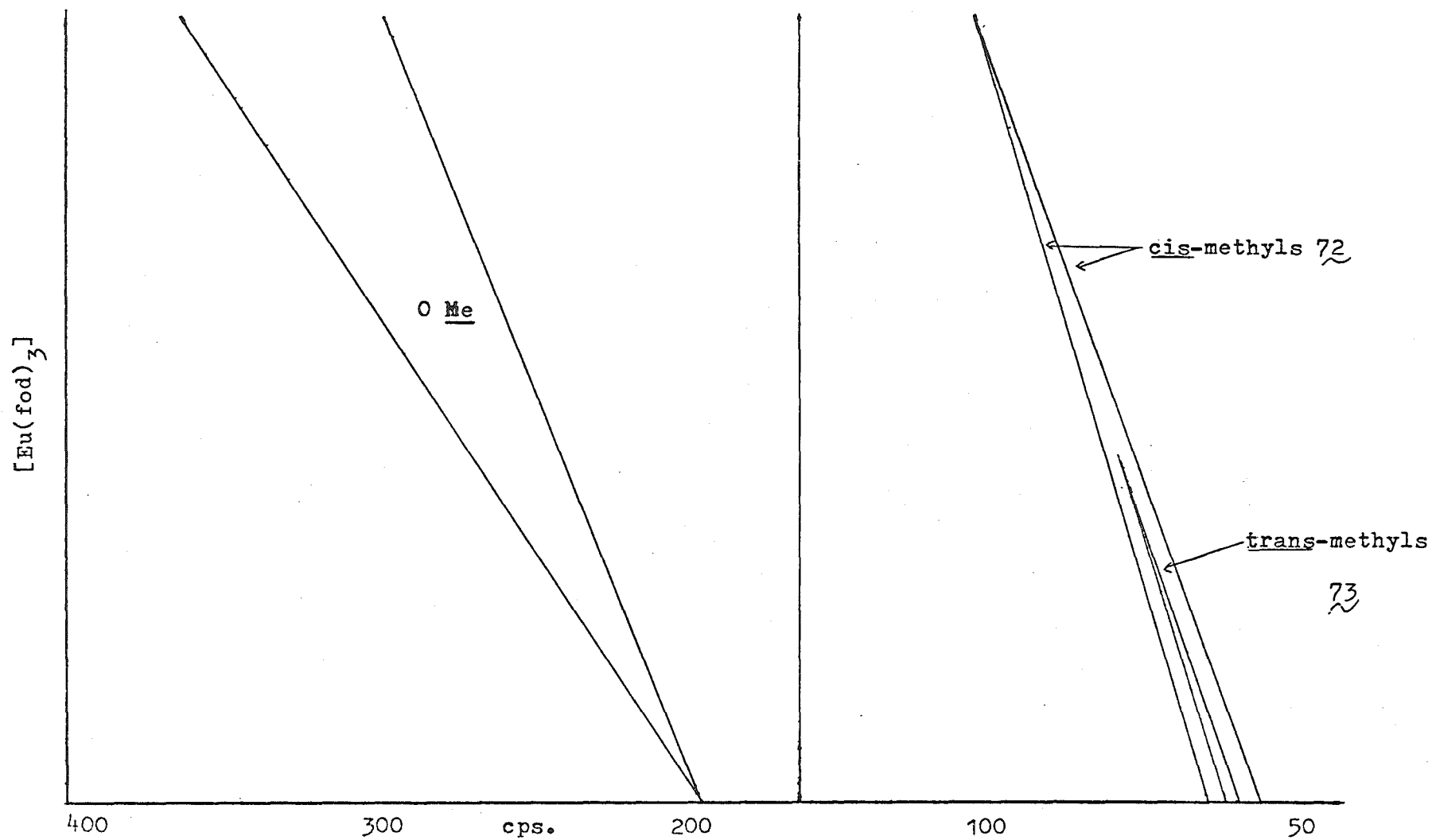
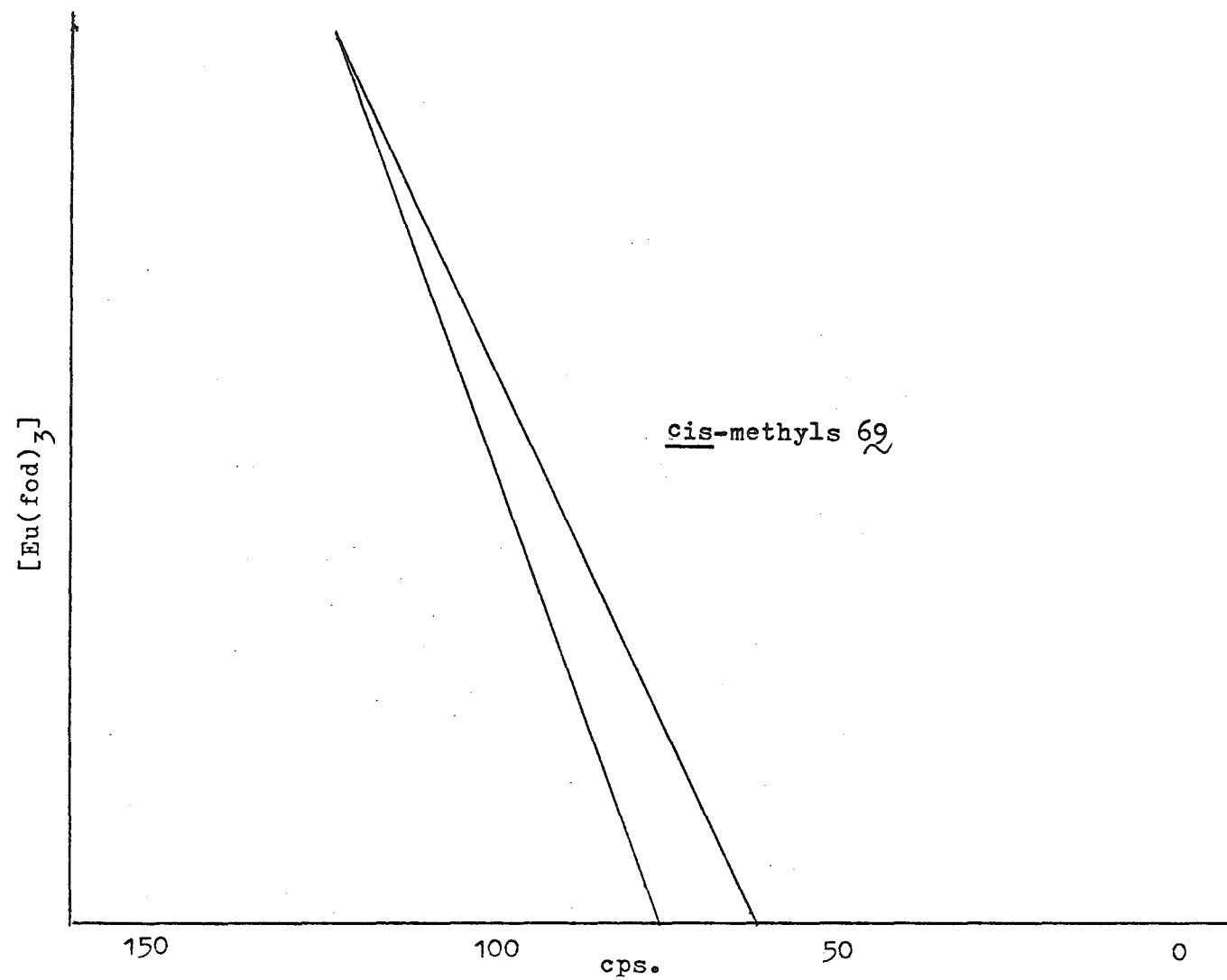
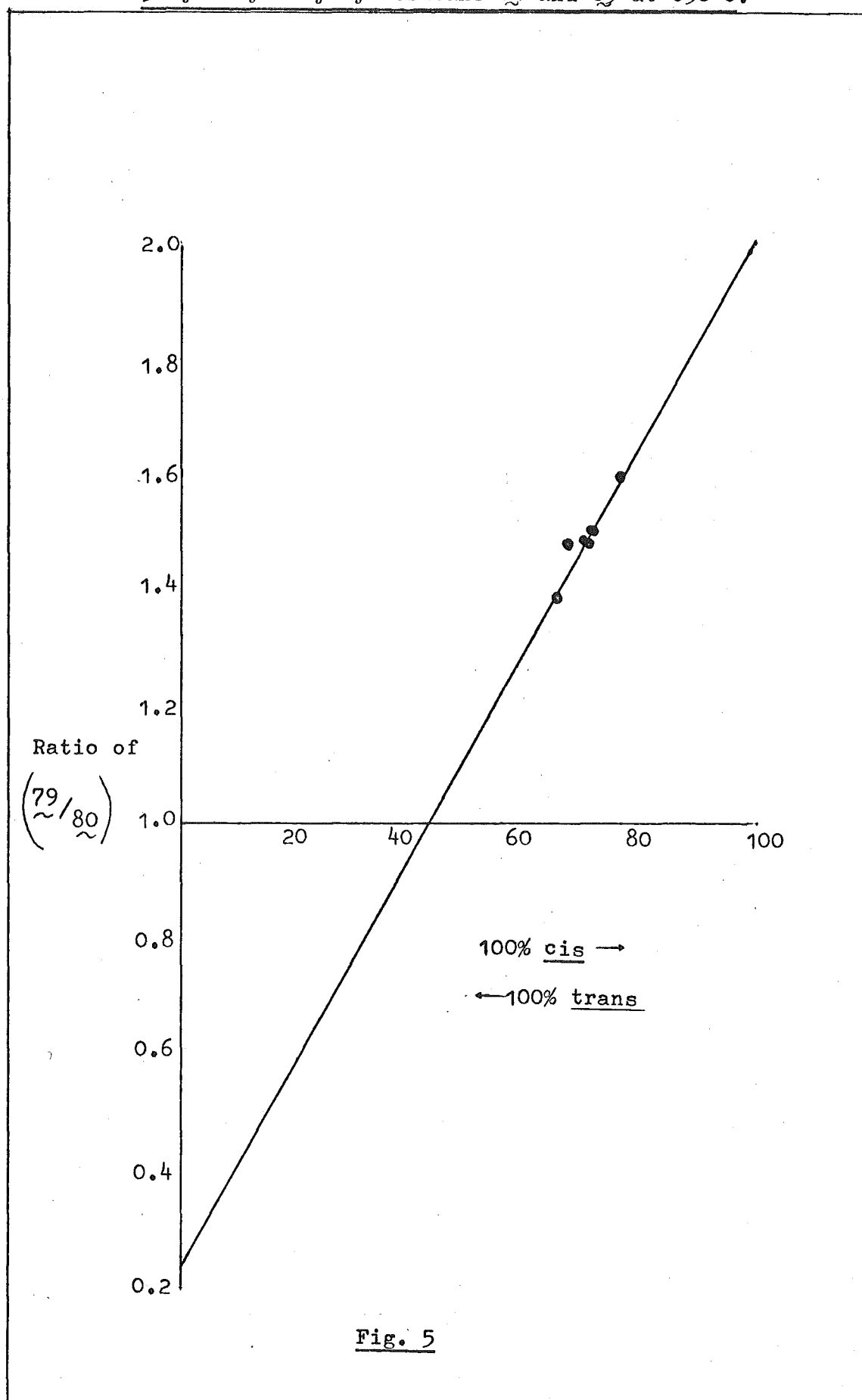


Fig. 4 Graph of $[\text{Eu}(\text{fod})_3]$ v's chemical shift of cis-pinic acid 69



Pyrolysis of cis and trans 2,2-dimethyl-1-(2-hydroxyethyl)-
3-hydroxymethylcyclobutane 64 and 65 at 650°C.



g.l.c. to contain a high proportion of low boilers (>74%), and two major products in addition to the starting material. The major products were identified as 1-methoxy-3-methylbut-2-ene $\tilde{70}$ and 1-methoxy-4-methylpent-3-ene $\tilde{71}$.

The n.m.r. spectrum of 1-methoxy-3-methylbut-2-ene $\tilde{70}$ exhibited two singlets centered at δ 1.68 and δ 1.75 due to the vinyl methyls and an -OCH_3 singlet centered at δ 3.32. The $(\text{C1})\text{H}_2$ was coupled to $(\text{C2})\text{H}$ ($J_{1,2} = 7$ Hz) and appeared as a doublet centered at δ 3.89. The $(\text{C2})\text{H}$ appeared as a triplet centered at δ 5.35 ($J_{1,2} = 7$ Hz). 1-methoxy-4-methylpent-3-ene $\tilde{71}$ exhibited two singlets centered at δ 1.65 and 1.73 due to the vinyl methyls. The -OCH_3 singlet centered at δ 3.37 was superimposed on the $(\text{C1})\text{H}_2$ triplet centered at δ 1.38 ($J = 7$ Hz). The $(\text{C3})\text{H}$ appeared as a triplet centered at δ 5.18 ($J_{3,2} = 7$ Hz) and the $(\text{C2})\text{H}_2$ appeared as a doublet of triplets centered at δ 2.25 ($J_{2,1} = J_{2,3} = 7$ Hz).

The ratio of yields of the products $\left(\frac{\tilde{70}}{\tilde{71}}\right)$ v's the percentage of cis- compound $\tilde{72}$ is shown in Fig. 6 and the line of best fit is drawn from regression analysis.

Pyrolysis of 1,3-disubstituted-2,2-dimethylcyclobutanes will involve initial cleavage of either of the bonds adjacent to the gem-dimethyls substituents as shown in Scheme 11. The transition states in going to the diradical intermediates are expected to be twisted. Fragmentation of the biradical can occur by cleavage of the opposite C-C bond leading to the formation of alkenes. It was only possible to isolate the alkenes containing the gem- dimethyls since these were higher boiling. The relative yields of dimethyl alkenes in each case gives a measure of the partitioning of the reactions between paths a and b.

Pyrolysis of cis- and trans- 2,2-dimethyl-1-(2-methoxyethyl)-
3-methoxymethylcyclobutane 72 and 73 at 630°C

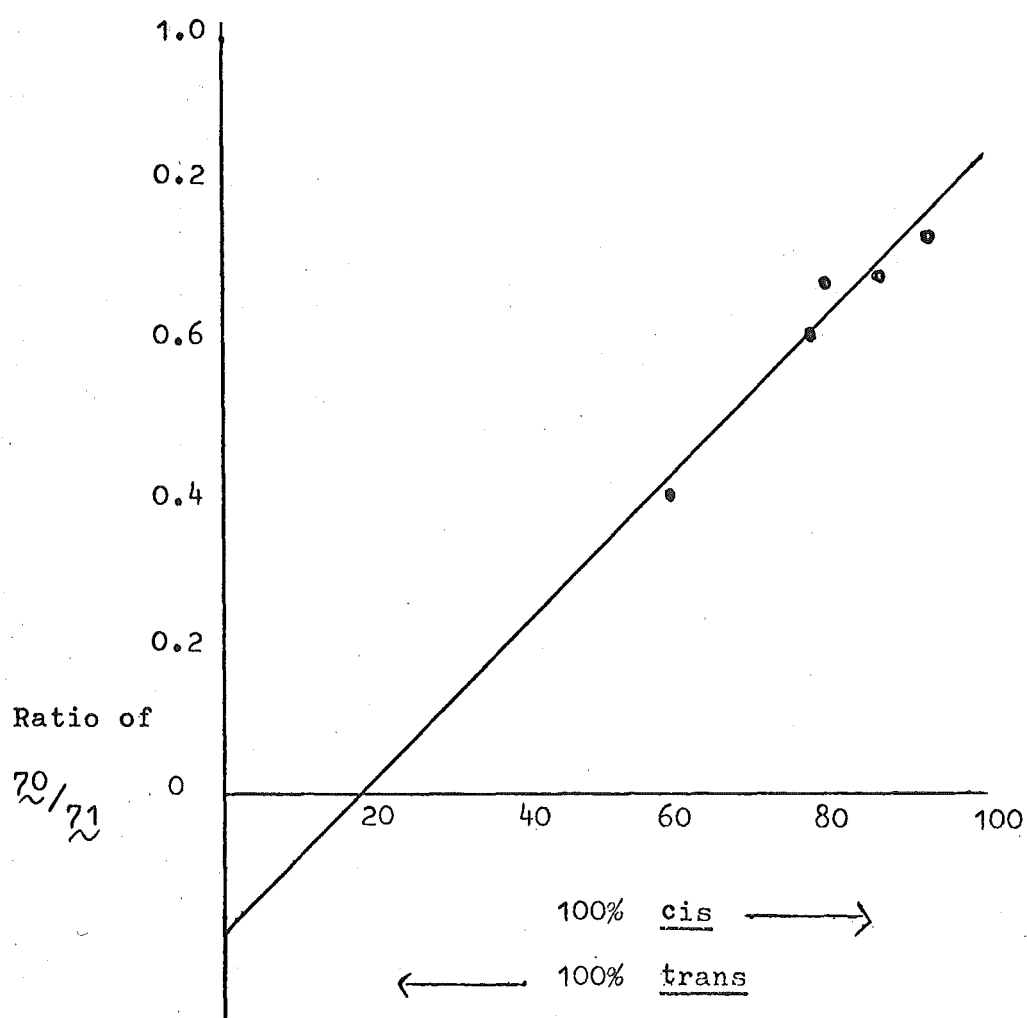
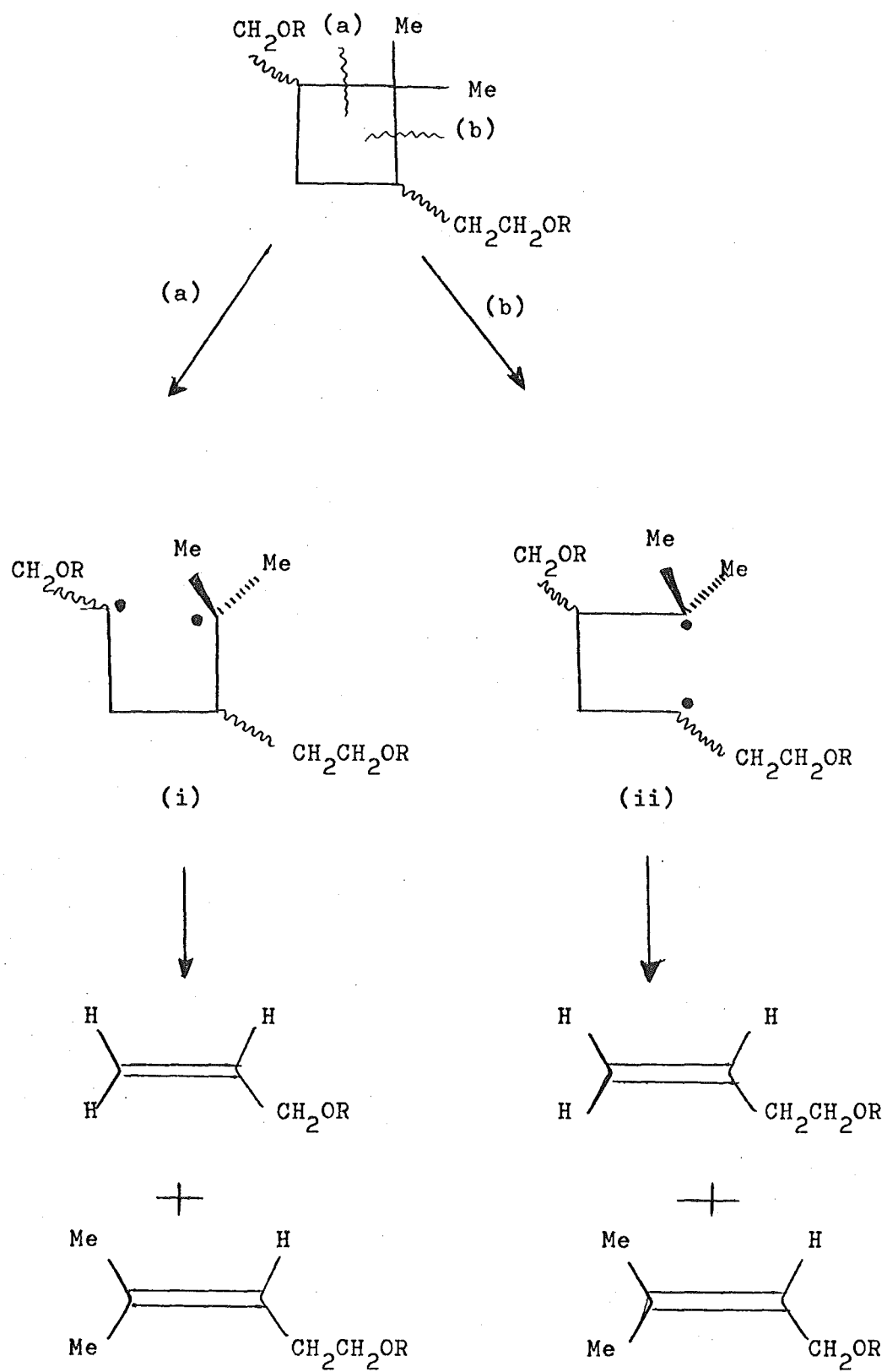


Fig. 6



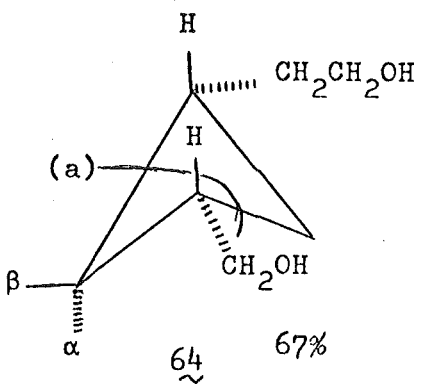
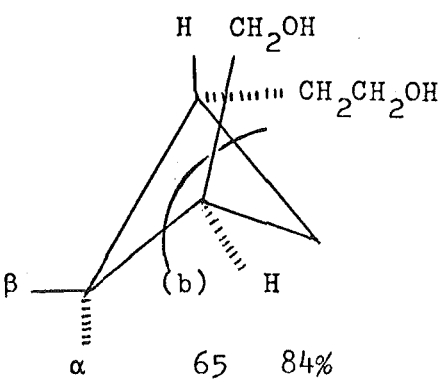
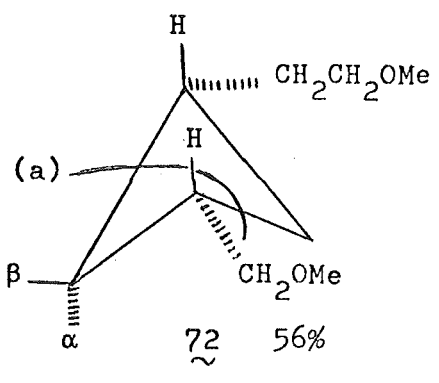
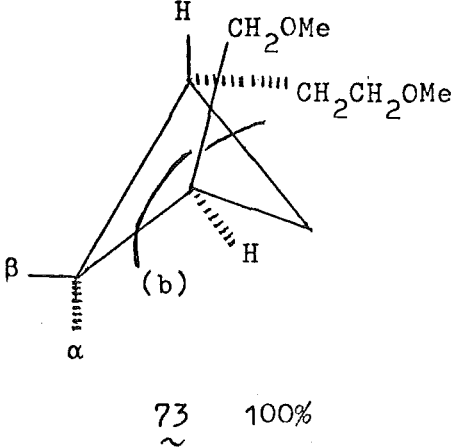
$\text{R} = \text{H} \text{ or } \text{Me}$

Scheme 11

The results of pyrolysis of the different isomeric mixtures of 64 and 65 and 72 and 73 are shown in Figs 5 and 6. Extrapolation to the pure isomers is shown using regression analysis. In Fig. 6 this results in an impossible negative value (-0.2) for the pyrolysis of the trans- isomer 73 . Within experimental error however this result allows for a 100% yield of 1-methoxy-4-methylpent-3-ene 71 from the trans- isomer 73 . The extrapolated results for the cis- and trans- isomers 64 , 72 , 65 and 73 are summarized in (Table 11). It must be realized however, that these results are obtained by extrapolation of the pyrolysis data obtained for mixtures of the cyclobutane isomers varying over a relatively small region. The results for the dimethoxy compounds 72 and 73 contain less error since a wider range of cis-: trans- isomeric mixtures were available.

For the cis- compounds 64 and 74 there is a slight preference for bond cleavage to occur adjacent to the more bulky substituent i.e. via path b. This bias for opening of the cyclobutane ring adjacent to the more bulky substituent ($\text{CH}_2\text{CH}_2\text{-OH}$ or $\text{-CH}_2\text{CH}_2\text{-OCH}_3$) is offset when the less bulky substituent (CH_2OH or CH_2OMe) is in an axial configuration. Pyrolysis of the trans- compounds 65 and 73 gives a high yield of 4-methylpent-3-en-1-ol (80 , ca 84%) and 1-methoxy-4-methylpent-3-ene (71 , ca 100%) respectively; cleavage occurring adjacent to the axial substituent (path a). The steric compression resulting from the axial configuration of the smaller oxygenated substituent is therefore important in determining the reaction pathway.

Table 11

	Ratio $\frac{a}{b}$
 <p>64 67%</p>	2.0 = 2:1
 <p>65 84%</p>	0.2 = 1:5
 <p>72 56%</p>	0.8 = 4:5
 <p>73 100%</p>	≈ 0 = 0:1

EXPERIMENTAL

Infrared spectra were recorded on a Shimadzu IR27G spectrophotometer and are for liquid films unless otherwise stated. N.M.R. spectra were obtained on a Varian T 60 spectrometer for CDCl_3 solutions with CHCl_3 and TMS as internal standards. Analytical gas chromatography was performed on a Varian 2100 using 2 $\frac{1}{2}$ % E.G.A. and Carbowax 20M, in glass columns. Preparative g.l.c. was performed on a Varian 706 and Pye 105 Chromatograph using 8% E.G.A. and 10% Carbowax 20M columns.

Nopinone 61

β -Pinene (20 g) was dissolved in methanol (180 mls.) in a 250 ml. round bottom flask fitted with a bubbler tube. The mixture was kept at -70°C in a dry ice acetone bath. Ozone in oxygen generated by Welsback Ozonator Model T-816 was passed through the solution until the effluent gas gave a strong colouration with moist starch iodide paper (ca $1\frac{1}{2}$ hours). The solution was poured into water (1 l.) and left overnight. Extraction with ether (3 x 100 mls.) and subsequent washing with water, until the washings no longer coloured starch iodide paper, gave, after evaporation and fractional distillation, nopinone 61 (14 g.) ν_{max} 1720, 1460, 1195, 1030 cm^{-1} . n.m.r. δ 1.33 (singlet, $(\text{C8})\text{H}_3$), 0.85 (singlet, $(\text{C9})\text{H}_3$) (lit. cit.,³⁷ 1.33 ($(\text{C8})\text{H}_3$), 0.85 ($(\text{C9})\text{H}_3$)).

Toluene-4-sulphonhydrazone of Nopinone 62

Nopinone (5 g.) was added to a mixture of toluene-4-sulphonhydrazine (6.5 g.) and p-toluene sulphonic acid (50 mg.) in methanol (10 ml.). The solution was warmed to 60° for 10 mins, then left for 10 mins. when crystallization was induced. The crystals were filtered and washed with cold petroleum ether. Recrystallization from methanol gave the hydrazone 62 (9 g.) as needles, m.p. $169 - 171^{\circ}\text{C}$. ν_{max} 1020 ($\text{S} = \text{O}$), 1450 ($\text{C} = \text{N}$), 3245 (N-H) cm^{-1} n.m.r. δ 1.23 ($(\text{C8})\text{H}_3$), 0.62 ($(\text{C9})\text{H}_3$), 2.43 (Ar-CH_3), 7.62 (quartet, $J_{\text{AB}} = 8 \text{ Hz}$, $\Delta\delta = 0.31$).

Decomposition of the Sodium Salt of Hydrazone 62

The sodium salt of hydrazone 62 was prepared by the method of W. M. Jones³⁸. The hydrazone (5 g.) was dissolved in 50 mls. of

dry tetrahydrofuran (T.H.F. distilled over CaH_2 and stored over molecular sieves), and one equivalent of sodium hydride (obtained as a 50% suspension in mineral oil) was added slowly with stirring. Stirring was continued for an additional 15 mins. Reagent-grade pentane (ca 300 mls.) was added and the resulting precipitate was filtered, dried in a vacuum dessicator, and stored in a dark bottle.

The sodium salt of the sulphonhydrazone was heated slowly in an oil bath to 160°C . (N.B. the temperature should not exceed 165°C otherwise exothermic decomposition to a black tar occurs.) The products of decomposition were removed under reduced pressure as they were formed and collected in a dry ice acetone trap. The crude product (ca 75% pure by g.l.c.) was purified by spinning band distillation to give norpinene 63 (ca 70% yield), ν_{max} 721 cm^{-1} n.m.r. δ 6.15 (multiplet, 1H, $W = 22\text{ Hz}$; ((C3)H), 5.54 (doublet of multiplets, 1H, $J_{2,3} = 8\text{ Hz}$; (C2)H), 1.28 (singlet, (C8)H₃), 0.90 (singlet (C9)H₃). (lit. cit.³¹ δ 6.15 (m., 1H, $w = 22\text{ Hz}$), 5.54 (doublet of multiplets, $J_{2,3} = 9\text{ Hz}$), 1.28 ((C8)H₃), 0.90 ((C9)H₃)).

Ozonolysis of Norpinene 63

Norpinene (3 g.) was dissolved in 200 mls of dry ether. The mixture was cooled in a dry ice acetone bath (ca -70°C) and ozone was bubbled through the solution until the effluent gases gave a strong colouration with moist starch iodide paper. Dry tetrahydrofuran (300 ml.) was added to the ozonide and the ether removed by distillation through a Vigreux column. Three equivalents of lithium aluminium hydride were slowly added to the ozonide with rapid stirring and cooling to keep the mixture at

room temperature. The mixture was heated under reflux for three days. Excess lithium aluminium hydride was removed by careful addition of hydrated crystals of sodium sulphate, followed by the addition of a few drops of water till the mixture formed a white precipitate. The solution was filtered, dried with anhydrous magnesium sulphate, and after removal of solvent gave an oil (0.5 g.) which was shown by t.l.c. on alumina to contain three compounds.

The product was adsorbed onto 5% deactivated alumina (20 g.) and elution with petroleum-ether-ether afforded cis- 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutane 64 (20 mg.).

ν_{\max} 3350, 2970, 1465, 1350, 1050 cm^{-1} , n.m.r. δ 0.95 (singlet, $\beta\text{-CH}_3$), 1.11 (singlet, $\alpha\text{-CH}_3$), 3.50 (multiplet, 4 H, $W_{h/2} = 18$ Hz) M^+ measured 158.131140 g. mol^{-1} , $\text{C}_9\text{H}_{18}\text{O}_2$ requires 158.130668 g. mol^{-1} .

cis- and trans- Pinonic acid 66 and 67.

(a) Oxidation using Potassium Permanganate.

A solution of potassium permanganate (233 g.) and ammonium sulphate (75 g.) in water (2 l.) was added slowly to a mixture of α -pinene (100 g.) and water (660 mls.) with rapid stirring. The mixture was kept at room temperature by cooling in an ice bath. After stirring for two hours, the excess potassium permanganate was destroyed by the addition of methanol and the mixture was filtered through celite "filter aid" on a Buchner funnel. The filtrate was acidified with dilute sulphuric acid and the organic material extracted with ether using a continuous extractor. The crude acid was purified by dissolving in dilute sodium hydroxide solution, acidifying with dilute sulphuric acid and then extracting with ether. The solvent was removed under vacuum to give a mixture of cis- and trans- pinonic acid (66 and

67) (30 g.). The n.m.r. spectrum indicated the mixture to be predominantly cis-3-acetyl-2,2-dimethylcyclobutylacetic acid

67. n.m.r. δ 0.90 (singlet, β -CH₃), 1.37 (singlet, α -CH₃), 2.1 (singlet, 3 H, CH₃-C-), 3.55 (doublet, J = 7 Hz), 2.0 - 3.0 (4 H). (Lit. cit.⁴⁷ n.m.r. δ 0.90 (singlet, β -CH₃); 1.37 (singlet, α -CH₃).

(b) Ozonolysis of α -Pinene.

To α -pinene (100 mls.) in a 1 l. flask was added carbon tetrachloride (300 mls.) and acetic acid (20 mls.). The mixture was cooled in an ice salt bath and ozone was bubbled through until the effluent gases gave a strong colouration with moist starch iodide paper. The volume of the mixture was reduced to approximately 100 mls. by heating on a water bath and then a mixture of acetic acid (150 mls.), water (100 mls), and hydrogen peroxide (50 mls.; 30%) was added. The solution was heated under reflux for one hour and hydrogen peroxide, (100 mls.; 30%) added and reflux continued for a further hour. The mixture was acidified with dilute sulphuric acid and the product extracted with ether. The crude product was purified as above to give mainly cis- pinonic acid (30 g.). n.m.r.

δ 0.90 (singlet, β -CH₃), 1.37 (α -CH₃), 2.1 (singlet, 3 H, CH₃-C-), 3.55 (doublet, J = 7 Hz), 2.0 - 3.0 (4 H). (Lit. cit.^{47,52} δ 0.90 (singlet, β -CH₃), 1.37 (singlet, α -CH₃).

Pinic Acid 68 and 69.

Bromine (20 g.) was added dropwise to a solution of sodium hydroxide (15 g.) in water (250 ml.). The solution was kept cool by immersion in an ice bath. A mixture of cis- and trans- pinonic acid (5 g.) dissolved in aqueous sodium hydroxide

(10 ml., ≈ 1 N) was added to the solution. After 5 min. bromoform started to separate. A small amount of sodium hydroxide (3 g.) was added and the mixture left to stand for two hours.

The mixture was then added to a cooled solution of sodium bisulphite and diluted sulphuric acid. Bromoform was removed by filtration. The water soluble filtrate was acidified with dilute sulphuric acid and the product was extracted with ether by continuous extraction. The crude acid was purified by dissolving in aqueous sodium hydroxide, acidifying with dilute sulphuric acid and extracting with ether. Removal of solvent afforded a thick oil (4 g.) shown by n.m.r. to be predominantly cis-pinic acid (69). n.m.r. cis-pinic acid δ 1.00 (β -CH₃), 1.25 (α -CH₃), 10.1 (singlet, 2 H, -OH), 2.0 - 4.0 (6 H), trans-pinic acid δ 1.09 (3 H), 1.12 (3 H). (Lit. cit.⁴⁷ δ 1.00 (singlet, β -CH₃), 1.25 (singlet, α -CH₃)).

cis- and trans-2,2-Dimethyl-1-(2-hydroxyethyl)-3-hydroxymethyl-
cyclobutane 64 and 65

A mixture of cis- and trans-pinic acid (5 g.) (68 and 69) was dissolved in dry ether (20 ml.) and added to a slurry of lithium aluminium hydride (5 g.) in dry tetrahydrofuran (200 mls.). The mixture was heated under reflux for three days. The excess lithium aluminium hydride was destroyed by the addition of hydrated crystals of sodium sulphate followed by a few drops of water. The mixture was filtered and the solvent was evaporated to give an oil (3 gm.) consisting mainly of 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutane. (cis:trans, 68:32). ν_{\max} 3350, 2975, 1465, 1350, 1050 cm⁻¹. n.m.r. cis- δ 0.95

(singlet, β -CH₃), 1.11 (singlet, α -CH₃), 3.50 (multiplet, 4 H, $W_{h/2} = 18$ Hz). trans- δ 1.00 (3 H), 1.05 (3 H). M^+ measured 158.131140 g. mol⁻¹, C₉H₁₈O₂ requires 158.130668 g. mol⁻¹. (Lit. cit.⁵³). For pyrolysis purposes the diol was purified by preparative gas liquid chromatography on a 10% Carbowax 20 M column. Enriched fractions of one or the other of the isomers (75:25, 72:28, 67:33, 65:35; cis:trans) were obtained this way.

Nitrosomethylurea⁵⁴

In a weighed 1 l. flask was placed aqueous methylamine solution, (200 g; 24%) and concentrated hydrochloric acid was added until the solution was acid to methyl red. Water was added to bring the total weight of the mixture to 500 g. Urea (300 g.) was added, and the solution was heated gently under reflux for two and three quarter hours and then vigorously for 15 minutes. The solution was cooled to room temperature, sodium nitrate (110 g; 95%) was added and the mixture cooled to 0°C. A mixture of ice (600 g.) and concentrated sulphuric acid (100 g.) in a 3 l. beaker was surrounded by an ice bath, and the cold methylurea-nitrite solution was added slowly with rapid mechanical stirring. The temperature was kept below 0°C.

Nitrosomethylurea rose to the surface as a crystalline foamy precipitate and was filtered immediately under vacuum and pressed onto the filter. The crystals were stirred to a paste with cold water (50 cc), sucked dry under vacuum and dried in a vacuum dessicator to constant weight, (103 g., 65% theoretical yield) and stored at 0°C.

Diazomethane⁵⁴

Aqueous potassium hydroxide solution (60 mls. of 50% W/V) and ether (200 mls.) was placed in a 500 ml. round bottom flask. The mixture was cooled to 5°C and nitrosomethylurea (20.6 g.) added with shaking. The flask was fitted with a condenser ready for distillation. The lower end of the condenser carried an adapter passing through a two-holed stopper and dipping below the surface of ether (40 ml.) contained in a 300 ml. Erlenmeyer flask cooled in an ice-salt mixture. The exit gases were passed through a second portion of ether (40 mls) also cooled below 0°C. The reaction flask was placed in a water bath at 50°C and brought to the boiling point of ether with occasional shaking. The ether was distilled till the distillate was almost colourless (i.e. after almost two thirds of ether had been distilled.). The combined ether solutions in the receiving flasks contained 5.1 g. of diazomethane (62% theoretical yield).

For analysis, the diazomethane-ether solution was allowed to react at 0°C with a solution containing 1.300 g. of A.R. benzoic acid in absolute ether (50 mls). The unreacted benzoic acid was titrated with standard sodium hydroxide solution (0.2 N).

Methylation of 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxy-
methylcyclobutane

A 68:32 mixture of cis- and trans- 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutane (64 and 65) was dissolved in dry ether (50 mls) and a stock solution of catalyst* (1 ml.) added. Diazomethane, dissolved in ether was added

slowly from a burette at the rate of 2 mls per minute. The reaction was very fast as seen by the immediate decolourization of the diazomethane and vigorous evolution of nitrogen. After addition of diazomethane, sufficient for the yellow colour to persist, additional catalyst (0.5 ml) was added and the mixture was left to stand for 4 hours. The mixture was filtered (to remove the small amount of polymethylene formed) and dried with anhydrous magnesium sulphate. The solvent was removed under a slight vacuum and t.l.c. of the product mixture on a silica plate showed three spots. The required product was isolated by dry column chromatography (silica) with chloroform as the eluent. Further purification by preparative gas liquid chromatography on a 8% E.G.A. column gave a mixture of cis- and trans- 2,2-dimethyl-1-(2-methoxyethyl)-3-methoxymethylcyclobutane (72 and 73). Analytical g.l.c. indicated a 78:22 mixture of cis and trans isomers, ν_{\max} 2920, 2850, 1390, 1360, 1110 cm^{-1} . n.m.r. cis- δ 0.90 ($\beta\text{-CH}_3$), 1.05 ($\alpha\text{-CH}_3$), 3.21 (singlet, 6 H, $-\text{O-CH}_3$). trans- δ 0.97, 1.02 (singlets, gem-dimethyls), 3.21 (singlet, 6 H, $-\text{O-CH}_3$). M^+ measured 186.161971 g. mol^{-1} , $\text{C}_{11}\text{H}_{22}\text{O}_2$ requires 186.161661 g. mol^{-1} .

* Catalyst Stock Solution

To anhydrous ether (19 mls.) in a 25 ml. volumetric flask at 0°C was added fluroboric acid (0.25 mls., 11 N). The volume was made to 25.0 mls. by the addition of methylene chloride.

Tosylation reaction of cis- and trans-2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutane with p-toluene-sulphonyl chloride

To a solution of 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutane (2.3 gm., 68:32, cis:trans) in dry pyridine (120 mls, distilled over potassium hydroxide) was added three equivalents of pure p-toluenesulphonyl chloride (10 gm.). The mixture was kept overnight at room temperature then poured into water (100 ml.) and ether (200 ml.) in a separating funnel and shaken vigorously. The aqueous layer was discarded and the ether layer was washed several times with sulphuric acid (2%).

The ether solution was dried with anhydrous magnesium sulphate and the solvent removed under vacuum, to give a thick oily liquid (2 g.). T.L.C. on an alumina plate showed three spots. The products were isolated by column chromatography on 5% deactivated alumina with ether-pentane solvent mixtures. The major fraction was identified as cis- and trans- 2,2-dimethyl-1-(2-hydroxyethyl)-3-tosyloxymethylcyclobutane 74 and 75, and was shown by n.m.r. to be a 70:30 mixture (cis:trans) ν_{\max} 3450, 1600, 1340, 1165, 1090, 950 cm^{-1} n.m.r. cis- δ 0.83 ($\beta\text{-CH}_3$), 1.02 ($\alpha\text{-CH}_3$), 2.42 (singlet, $\phi\text{-CH}_3$), 3.39 (triplet, 2 H, $J = 7$ Hz), 3.94 (doublet, $J = 7$ Hz, $\text{CH}_2\text{-OTs.}$), 7.50 (quartet, $J_{AB} = 9$ Hz, $\Delta\delta = 0.21$). trans- δ 0.93 (3 H), 0.98 (3 H). (Found: C, 58.53; H, 7.10; S, 9.60. $\text{C}_{16}\text{H}_{24}\text{O}_4\text{S}$ requires C, 61.54; H, 7.69; S, 10.26%). The minor products were identified as; 2,2-dimethyl-1-(2-tosyloxyethyl)-3-tosyloxymethyl-cyclobutane 76; ν_{\max} 1600, 1340, 1170, 1090, 940, 670 cm^{-1} . n.m.r. δ 0.72 - 1.1 (6 H), 2.42 (singlet, 6 H, Ar-CH_3), 3.90 (multiplet, 4 H), 7.55 (quartet, $J_{AB} = 9$ Hz, $\Delta\delta = 0.20$).

(Found: C, 58.60; H, 6.62; S, 12.91; $C_{23}H_{30}O_6S_2$ requires C, 59.23; H, 6.44; S, 13.73%) and a mixture of cis and trans -2,2-dimethyl-1-(2-chloroethyl)-3-chloromethylcyclobutane (77 and 78) ν_{\max} 1450, 1350, 1275, 1255, 1160, 730, 690, 660 cm^{-1} . n.m.r. cis: δ 0.99 ($\beta\text{-CH}_3$), 1.15 ($\alpha\text{-CH}_3$), 3.4 (multiplet, 4 H). trans: δ 1.09 (6 H). Found: C, 56.33; H, 8.22; $C_9H_{16}Cl_2$ requires C, 55.38; H, 8.21. (Lit. cit.⁵⁵C, 55.21; H, 8.12.)

2,10-epoxy-10 β -Pinane 57

To a solution of β -pinane (5 g.) in dry ether (250 mls) was added meta-chloroperbenzoic acid (6.7 g.) and the mixture stirred at room temperature for 18 days. The mixture was poured into ether-water and washed several times with dilute sodium hydroxide solution and then further washed with water. The ether layer was dried with anhydrous magnesium sulphate, filtered and the solvent removed. The product was adsorbed onto alumina and elution with ether-pentane gave 2,10-epoxy-10 β -pinane (3.5 g.). n.m.r. δ 0.92 ($(C_9)H_3$), 1.24 ($(C_8)H_3$), 2.68 (quartet, 2 H, $J_{AB} = 5 \text{ Hz}$, $\Delta\delta = 0.2 \text{ ppm}$). (Lit. cit.⁵⁰ δ CCl_4 0.92 ($(C_9)H_3$), 1.23 ($(C_8)H_3$)).

10 β -Pinane-2,10-diol 47

A solution of potassium permanganate (100 g.) and magnesium sulphate (75 g.) in water (2 l.) was added dropwise to a stirred solution of β -pinene (100 g.) in ethanol (1.5 l.). The temperature was kept below 5°C by immersion in an ice-salt bath. After two hours the mixture was filtered through celite "filter aid" on a Buchner funnel. The filtrate was reduced in volume by distillation until the vapour reached a temperature of 99°C.

Salt was added to the residue and product diol was extracted with ether using a continuous extractor. After removal of the solvent the diol was adsorbed onto 10% deactivated alumina. Elution with ether-pentane gave 10 β -pinane-2,10-diol 47 (7.5 g.). m.p. = 73 - 75°C. ν_{\max} 3280, 2900, 1465, 1388, 1368, 1235, 1218, 1059 and 1033 cm^{-1} (CHCl_3 soln.) n.m.r. δ 0.93 ((C9)H₃), 1.27 ((C8)H₃), 3.52 (s, (C10)H₂-OH). (Lit. cit.⁶ δ CCl_4 0.93 (3 H), 1.26 (3 H).

Pyrolysis

A variety of procedures have been used to pyrolyse compounds in the vapour phase but the most effective involves use of a continuous flow apparatus with short contact times. The pyrolysis apparatus used for this work consisted of a 38 cm. long stainless steel tube (2.3 mm. i.d.), which contained a steel rod (1.6 mm. i.d.), giving a cross-sectional reactor space area of 0.0179 cm^2 . The stainless steel tube was contained in another tube (1/8" i.d.) and this was surrounded by heating coils connected to a rheostat. The apparatus was insulated by vermiculite contained in a hollow glass tube and was calibrated over a temperature range $200^\circ - 600^\circ$ by a standardized Pt/Rh thermocouple.

The injector block had a carrier gas (oxygen free nitrogen) inlet with separate heater and could be heated to 240°C . The injection rate was controlled by using a micrometer syringe which was equipped with electrical heating facilities for use with solid samples. The pyrolysate was collected in U tubes which were cooled in a dry ice acetone bath.

Pyrolysis of 10 β -Pinane-2,3 α -diol 48

10 β -Pinane-2,3 α -diol 48 was pyrolysed at 450°, 500°, and 600°C with an injection rate of 250 μ l/min and a carrier gas flow rate of 15 mls/min. The crude product (ca 90%) was shown by g.l.c. to contain more than thirteen compounds. In addition to the starting material, two main products were isolated by preparative g.l.c. and identified as;

- (i) 2,2,3-trimethylcyclopent-3-ene-1-acetaldehyde 49 (18, 20, 25%). ν_{\max} 1725, 2750 cm^{-1} . n.m.r. δ 0.80 (singlet, CH₃), 1.00 (singlet, CH₃), 1.65 (singlet, (C3)CH₃), 5.29 (singlet, (C4)H, $W_{h/2} = 6$ Hz), 9.83 (triplet, CHO, $J = 2$ Hz). (Lit. cit. ²⁸ δ 0.78 (3 H), 1.00 (3 H), 1.65 (3 H), 5.26 (1 H), 9.78 (1 H)).
- (ii) 10 α -pinan-3-one 50 (20, 25, 27%), ν_{\max} 1710 cm^{-1} . n.m.r. δ 0.92 (singlet, (C9)H₃), 1.37 (singlet, (C8)H₃), 1.10 (doublet, $J = 7$ Hz, (C10) α -CH₃). The n.m.r. spectra was identical to an authentic sample.²⁸ A minor fraction (5, 10, 13%) was isolated but could not be identified and is thought to be a mixture of two compounds which do not separate on g.l.c. ν_{\max} 3500, 3000, 2750, 1720, 1700 cm^{-1} . n.m.r. δ 0.88 (3 H), 2.40 (6 H).

Pyrolysis of 2,3-epoxy-10 β -Pinane 51

The pyrolysis of 2,3-epoxy-10 β -pinane 51 at 500° and 600° was similar to the pyrolysis of 10 β -pinane-2,3 α -diol 48. The two major products were identified as 2,2,3-trimethylcyclopent-3-ene-1-acetaldehyde 49 (36, 40%) and 10 α -pinan-3-one 50 (38, 37%) in all respects identical with authentic samples.

Pyrolysis of 10 β -Pinane-2,10-diol 47

10 β -Pinane-2,10-diol 47 was pyrolysed at 500° and 600°, with

a carrier gas flow of 15 mls/min and an injection rate of 250 μ l/min. The crude product (ca 90%) contained four major products the yields of which were estimated by g.l.c. using Chromalog 1 Digital Integrator. Three of the major components were isolated by preparative g.l.c. and were identified as;

(i) 10 α -Pinan-10-al (31, 33%). ν_{\max} 1720, 2700 cm^{-1} n.m.r. δ 0.88 (singlet, (C9)H₃), 1.25 (singlet, (C8)H₃), 9.60 (doublet, J = 3 Hz, CHO). (Lit. cit.²⁷)

(ii) Myrtenol 59, (10, 15%), ν_{\max} 3400 cm^{-1} . n.m.r. δ 1.30 (singlet, (C8)H₃), 0.83 (singlet, (C9)H₃), 4.0 (singlet, $W_{h/2}$ = 4 Hz, (C10)H₂), 5.43 (singlet, $W_{h/2}$ = 7 Hz, olefinic proton). (Lit. cit.³¹ δ 5.45 (multiplet, $W_{h/2}$ = 6.5 Hz, (C 3)H), 3.95 (multiplet, $W_{h/2}$ = 4 Hz, (C2)H₂), 1.29 ((C8)H₃), 0.83 ((C9)H₃).

(iii) Perillyl alcohol 60, (20, 21%); ν_{\max} 3350 cm^{-1} . n.m.r. δ 1.73 (singlet, vinyl methyl), 4.73 (singlet), $W_{h/2}$ = 4 Hz, =CH₂), 4.0 (singlet, $W_{h/2}$ = 4 Hz, (C10)-CH₂-OH), 5.75 (multiplet, $W_{h/2}$ = 8 Hz, (C3) olefinic proton). (Lit. cit.³¹ δ 5.73 (multiplet, $W_{h/2}$ = 7 Hz), 4.73 (singlet, 2 H), 4.00 (singlet, 2 H, $W_{h/2}$ = 3 Hz, (C10)H₂, 1.75 (triplet, 3 H, J = J¹ = 1 Hz; (C9)H₃)).

Pyrolysis of 2,10-Epoxy-10 β -Pinane 57

Pyrolysis of 2,10-epoxy-10 β -pinane 57 gave similar products to 10 β -pinane-2,10-diol 47 but the ratio of products differed. The major product was identified as 10 α -pinan-10-al 58 (70, 71%) by comparison of n.m.r. and I.R. spectra with authentic samples. The two minor products were shown by g.l.c. analysis to be myrtenol 59 (3, 2%) and perillyl alcohol 60, (9, 8%).

Pyrolysis of cis-Myrtanol 83

cis-Myrtanol 83 prepared by E. Danstead²⁷ was pyrolysed at 500 and 600°C with an injection rate of 250 μ l/min and a carrier gas flow rate of 15 mls/min. The crude product (ca 95%) was shown by g.l.c. to contain more than four compounds in addition to the starting material (88 and 35%). The main product was isolated by preparative gas liquid chromatography on 2 $\frac{1}{2}$ % E.G.A. column and identified as 7-methylocta-1,6-diene-3-carbinol 84 (7, 48%). ν_{\max} 3400, 2940, 910 cm^{-1} . n.m.r. δ 1.60 and 1.67 (singlets, vinyl methyls), 3.50 (multiplet, $-\text{CH}_2-\text{OH}$), 4.9 - 5.5 (multiplet, 4 H, olefinic protons). The accurate mass of the parent ion was measured as 154.136145 g. mol^{-1} , $\text{C}_{10}\text{H}_{18}\text{O}$ requires 154.135758 g. mol^{-1} .

Pyrolysis of cis- and trans- 2,2-dimethyl-1-(2-hydroxyethyl)-
3-hydroxymethylcyclobutane 64 and 65.

Pyrolysis of different ratios of cis- and trans- 2,2-dimethyl-1-(2-hydroxyethyl)-3-hydroxymethylcyclobutane 64 and 65 at (600, 650 and 675°C) with an injection rate of 250 μ l/min and a carrier gas flow of 15 mls/min, gave a crude product (ca 70%), shown by g.l.c. to contain a very high percentage (ca 50%) of low boilers and two main products in addition to the starting material. The two products were isolated by preparative g.l.c. on 8 $\frac{1}{2}$ % E.G.A. column and identified as;

- (i) 4-methylpent-3-en-1-ol 80 ν_{\max} 3360, 1450, 1050 cm^{-1} . n.m.r. δ 1.67, 1.75 (vinyl methyls), 1.42 (OH), 2.28 (doublet of triplets, $J_{2,3} = J_{1,2} = 7$ Hz, $(\text{C2})\text{H}_2$), 3.63 (triplet, $J_{2,1} = 7$ Hz, $(\text{C1})\text{H}_2$), 5.17 (triplet, $J_{3,2} = 7$ Hz, $(\text{C3})\text{H}$).

The accurate mass could not be determined because of

instrumental fault, but the mass spectra showed a strong M^+ peak at 100. $C_6H_{12}O$ requires 100.15660.

(ii) 3-methylbut-2-en-1-ol 79. ν_{\max} 3350, 1450, 1000 cm^{-1} .
 n.m.r. δ 1.68, 1.75 (vinyl methyls), 2.29 (OH), 4.11 (doublet, $J_{12} = 7$ Hz, $(C1)H_2$), 5.43 (triplet, $J_{21} = 7$ Hz, $(C2)H$). The accurate mass could not be determined, but the mass spectra showed a strong M^+ peak at 86. $C_5H_{10}O$ requires 86.130.

Table 12

Ratio of yields of products ($\frac{79}{80}$) from the pyrolysis
of mixtures of 64 and 65 at 650°C.

<u>64</u>	<u>65</u>	<u>Ratio $\frac{79}{80}$</u>	
75.15	24.85	1.600	
71.50	28.40	1.519	
66.70	33.30	1.488	
65.40	34.60	1.387	
70.60	29.40	1.487)
		1.531) A.V. 1.495
		1.412) S.D. 0.053
		1.569)
		1.477)

Table 13

Ratio of yields of products ($\frac{79}{80}$) from the pyrolysis
75.15 : 24.85 mixture of 64 : 65.

<u>Temp.</u>	<u>Ratio $\frac{79}{80}$</u>
600°	0.933
650°	1.600
675°	2.219

N.B. The diol did not pyrolyse below 600°C.

Pyrolysis of cis- and trans- 2,2-dimethyl-1-(2-methoxyethyl)-
-3-methoxymethylcyclobutane 72 and 73

Different mixtures of cis- and trans- 2,2-dimethyl-1-(2-methoxyethyl)-3-methoxymethylcyclobutane 72 and 73 were pyrolysed at 630°C with an injection rate of 250 μ l/min and a carrier gas flow of 15 mls/min. The crude product (ca 70%) was shown by g.l.c. to contain a high proportion of low boilers (>40%), and two major products in addition to the starting material. The two products were isolated by preparative g.l.c. and identified as;

- (i) 1-methoxy-4-methylpent-3-ene 71. n.m.r. δ 1.65, 1.73 (singlets, vinyl methyls), 2.25 (doublet of triplets, $J_{2,3} = J_{1,2} = 7$ Hz, (C2)H₂), 3.38 (triplet, $J_{2,1} = 7$ Hz, (C1)H₂, superimposed by O-CH₃ singlet), 5.18 (triplet, $J_{3,2} = 7$ Hz, (C3)H).
- (ii) 1-methoxy-3-methylbut-2-ene 70. n.m.r. δ 1.68, 1.75 (singlets, vinyl methyls), 3.32 (singlet, O-CH₃), 3.89 (doublet, $J_{1,2} = 7$ Hz, (C1)H₂), 5.35 (triplet, $J_{2,1} = 7$ Hz, (C2)H).

Table 14

Ratio of yields of products ($\frac{72}{73}$) from the pyrolysis

of mixtures of $\frac{72}{73}$ and $\frac{73}{73}$ at 630°C.

<u>$\frac{72}{73}$</u>	<u>$\frac{73}{73}$</u>	<u>Ratio $\frac{72}{73}$</u>
92.53	7.47	0.73
86.00	14.00	0.68
79.32	20.67	0.67
77.25	22.75	0.60
58.50	41.50	0.39

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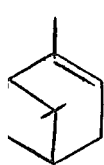
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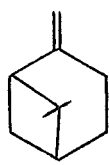
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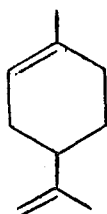
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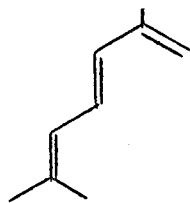
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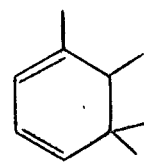
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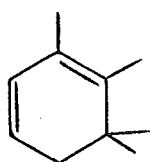
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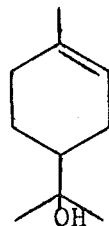
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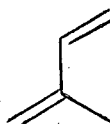
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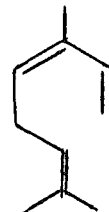
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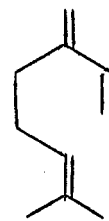
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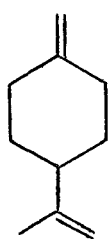
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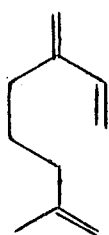
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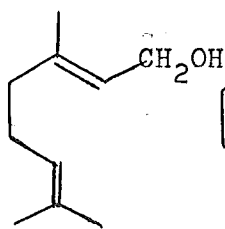
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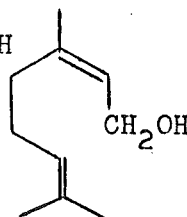
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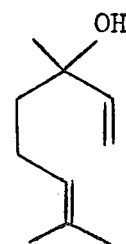
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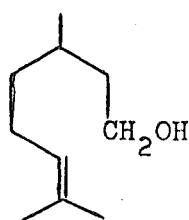
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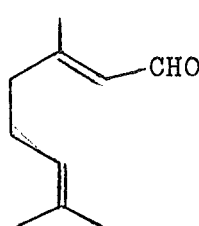
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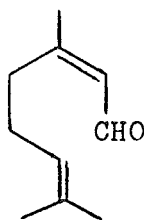
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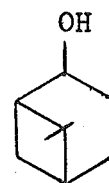
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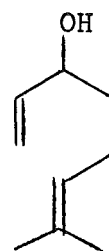
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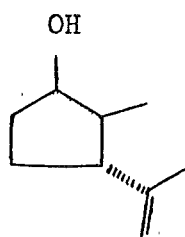
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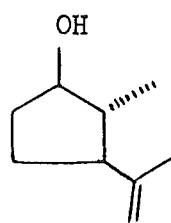
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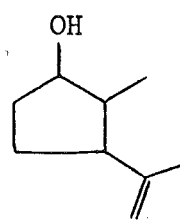
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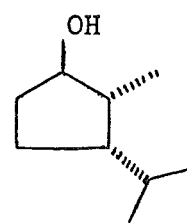
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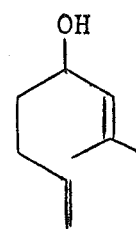
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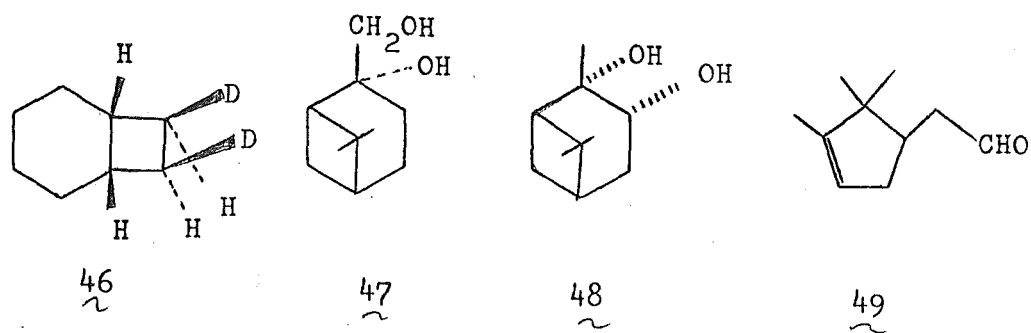
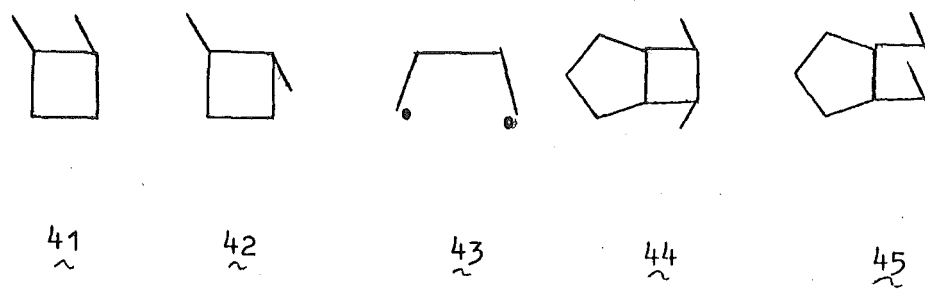
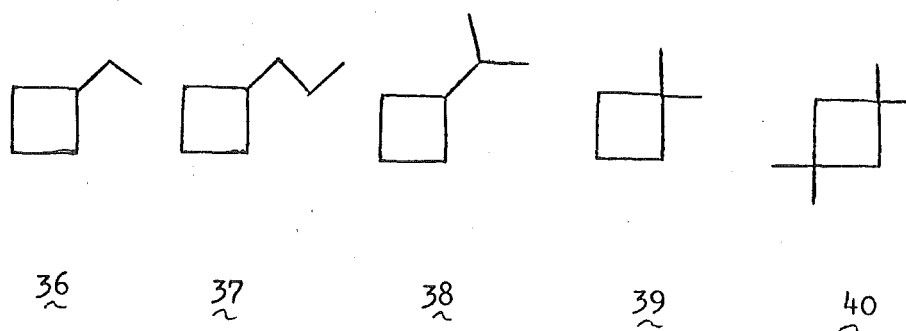
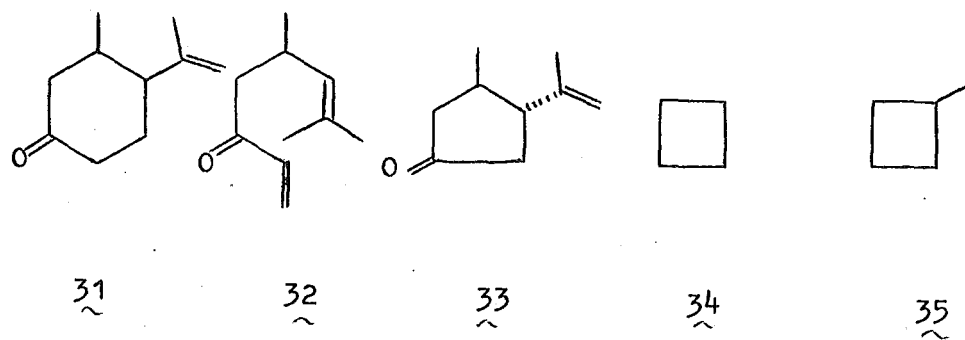
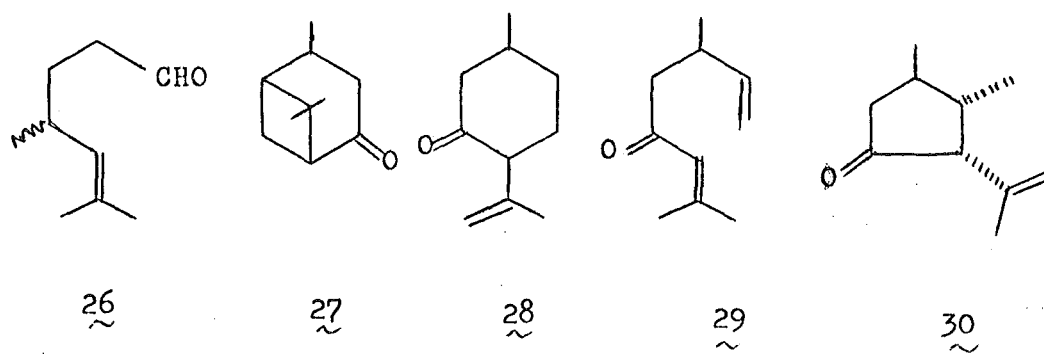
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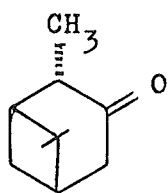
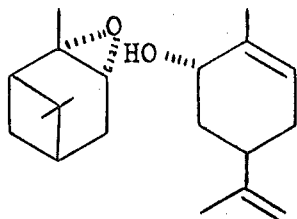
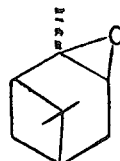
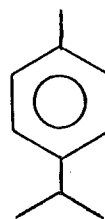
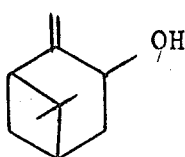
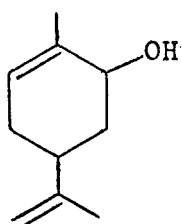
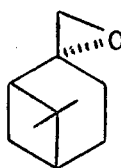
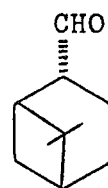
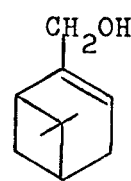
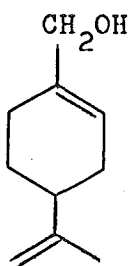
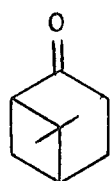
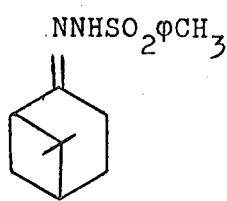
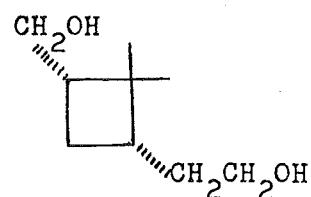
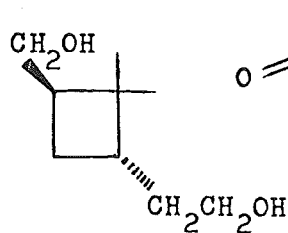
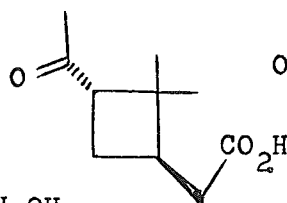
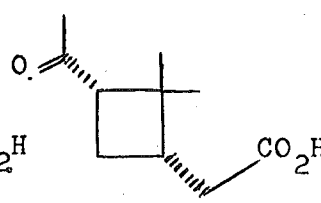
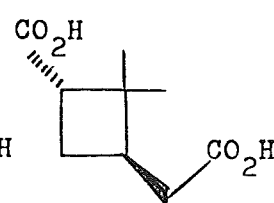
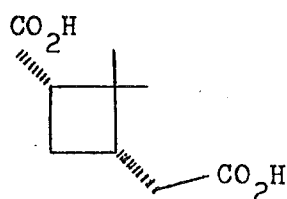
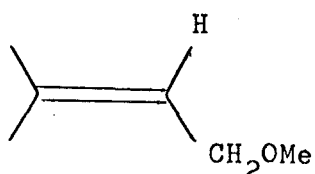
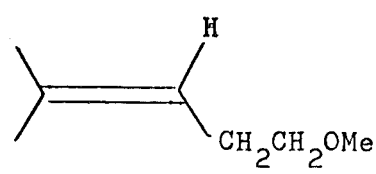


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